Face selectivity in the photocycloaddition reactions of acrylonitrile to 5-substituted adamantan-2-ones and pyrolysis of the products to methyleneadamantanes

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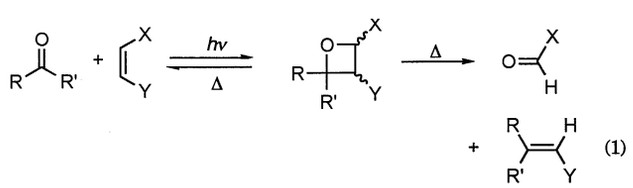
The photocycloaddition of acrylonitrile to 5-substituted adamantan-2-ones (1-X) produces two geometrically isomeric oxetanes in which the oxygen atom and the 5-substituent are in the *anti* or *syn* positions. The substituent was varied from fluoro, chloro, bromo, hydroxy to phenyl and the product ratios were similar (*ca.* 60:40) in all instances. Small portions (<5%) of the oxetanes were pyrolysed when analysed by GC at above 200 °C, and the products from the pyrolysis were confirmed to be the corresponding methyleneadamantanes by independent syntheses. Assignment of the configuration of the oxetanes was found to be consistent with ^{13}C additivity scheme and the chemical shifts are more closely predicted using known oxetanes of 1-X with methacrylonitrile. The product formation bias resulting from the attack on the *syn*-face can be explained using the Cieplak transition state theory.

Introduction

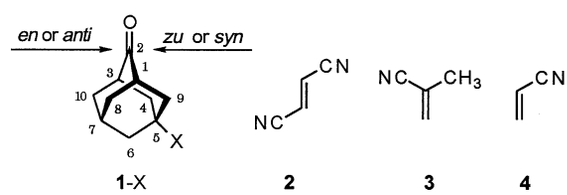
It is now recognized that transition state hyperconjugation, torsional and electrostatic effects are important in determining π-facial selectivity.[1–6] Although several model studies have clearly demonstrated the importance of long-range electronic effects to be a determining factor in diastereofacial selectivity, the precise nature of the electronic interaction remains controversial.[1–6] The symmetry of 5-substituted adamantan-2-ones **1**-X and their derivatives makes them useful probes for investigating the electronic effects on transition state energy since both faces of the carbonyl are little affected by steric effects of substitution at C-5.[3] Although torsional effects are involved in the transition state of nucleophilic (or electrophilic) addition to **1**-X, they are cancelled out due to the symmetry of the system allowing electronic effects to dominate in determining facial selectivity.[2b,3]

The photocycloaddition of ketones to olefins, also known as the Paterno–Büchi reaction,[7] is one of the earliest reported organic photochemical reactions.[8] The reaction was long neglected, as the product oxetanes seemed to be of little interest or value. However, in the past 10 years, this reaction has proved to be of considerable synthetic utility.[8c–g] Most of the oxetanes may undergo a thermal retro [2 + 2] cleavage at relatively low temperatures [eqn. (1)]. In some cases this thermal cyclo-



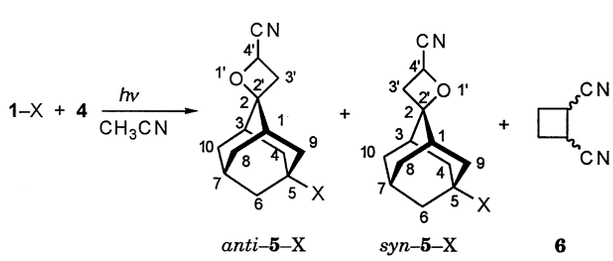
reversion leads to unsaturated long-chain compounds that are otherwise accessible only with much greater difficulty, especially in the case of bicyclic oxetanes derived from carbonyl compounds and cyclic alkenes.†

Recently, we have reported[9a] that photocycloaddition of the electron-poor olefins (*E*)-1,2-dicyanoethylene **2**, and methacrylonitrile **3** to 5-substituted adamantanones leads to oxetanes stereoselectively.[9a,c] Relative fluorescence quenching rates of **1**-H by several α,β-unsaturated nitriles **2**–**4** have been reported[10] to be **2**:**3**:**4** = 10:1.1:2; however, their products and face selectivities have not been fully explored. Thus, we report here our studies on the photocycloaddition of **1**-X to acrylonitrile **4** and pyrolysis of the products to methyleneadamantanes in GC at ⩾200 °C.



Results and discussion

The singlet n,π* state of **1**-X is trapped by acrylonitrile **4** *via* a concerted [2 + 2] cycloaddition involving the now occupied π* orbital which lead to a regiospecific reaction. The triplet state of **1**-X does not lead to an oxetane but results in olefin dimerization (Scheme 1). Exciplex formation has been proposed to be



Scheme 1

the initial step of a quenching interaction between ketone n,π* singlet or triplet states and olefins.[8a,b] The exciplex appears to have a charge transfer characteristic, with the n,π* state acting as an electron donor to electron-poor olefin (**4**).[8a,b] Once formed, the exciplex is subject to dissociation, or to bond formation leading directly to oxetanes.

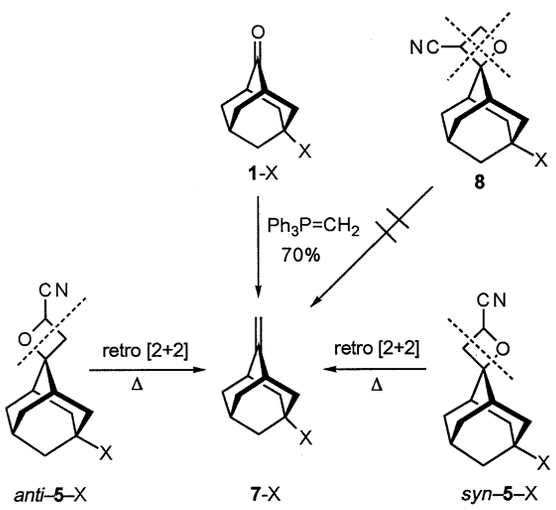
Irradiation (300 nm) of an acetonitrile solution of **1**-F and excess **4** in a Rayonet photoreactor gave two oxetanes in the

† In some cases this thermal [2 + 2] cycloreversion is also called a carbonyl–olefin-metathesis (COM) by Jones.[8e] For leading references see: T. S. Cantrell and A. C. Allen, *J. Org. Chem.*, 1989, **54**, 135; 140.

Table 1 *anti*:*syn* epimer ratios (%) in the photocycloadditions of **4** to 5-substituted adamantanones (**1**-X)[a] in acetonitrile at room temp.

5-Substituent X	*anti*-**5**-X	*syn*-**5**-X	Analysis
F	60	40	GC, NMR[b]
Cl	62	38	GC, NMR
Br	57	43	GC, NMR
C_6H_5	62	38	GC, GCMS
	57	43	NMR
OH	61	39	GC

[a] Error limit for GC and ^{13}C NMR analysis is ±5% due to pyrolysis at high temperature. Yields are *ca*. 70–90% based on converted **1**-X. [b] The inverse gated decoupling method was used for ^{13}C NMR measurement with a 60 s delay.



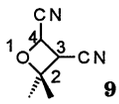
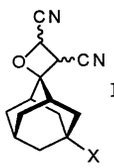
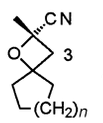
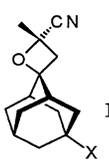
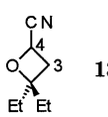
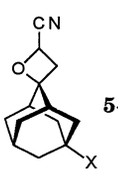
Scheme 2

ratio of 60:40 (see Scheme 1). Due to poor resolution of the two ABX ring-proton systems (*i.e.* CH_2C*H*CN) in ^{1}H NMR spectra, we used GC and ^{13}C NMR spectroscopy to determine the relative ratio of all oxetanes (see Table 1). Yields of oxetanes were ⩾70%, based on converted **1**-X; dimers **6** and polymers of **4** were also produced. An additional peak was observed in the products of the reaction of each **1**-X when analysed by GC; such a phenomenon has not previously been observed in the oxetane products of **1**-X with other α,β-unsaturated nitriles[9] even at higher analysing temperatures, *e.g.* ⩾240 °C. However, since ^{1}H NMR spectra of crude reaction products did not show any new peaks other than oxetanes, we later proved those new peaks in GC to be the pyrolysed products of **5**-Xs; *i.e.* 5-substituted 2-methyleneadamantanes **7**-Xs. The structures of **7**-X were proved by independent syntheses from the Wittig reaction of **1**-X (see Scheme 2 and Experimental section). The observation of **7**-X also implies the formation of **5** rather than those, **8**, from the alternative orientation of cycloaddition.

The mass spectra of the oxetanes are also given in the Experimental section. They generally showed weak molecular ions (0–30% by the EI method); the main fragments arise from fission across the oxetane ring. Such ring fission is a known process;[9,11,12] thus, the parent oxetane predominantly gives methyleneadamantanes **7**-X *via* ring cleavage just as that observed in GC analysis (*vida supra*).[12,13] The possible alternative structures **8** were eliminated from consideration by the lack of a large peak at *m*/*z* corresponding to the loss of HCOH from the molecular ion. Peaks at *m*/*z* corresponding to the loss of O=C(CN)H are clearly observed, also supporting the formation of oxetane structure **5**.

^{1}H NMR spectra again confirmed the structures **5**, rather than **8**. It has been reported[14] that hydrogen on the carbon α to the oxygen of an oxetane ring has a chemical shift of 4–5 ppm, whereas hydrogen on the β-carbon atom has a chemical shift of

Table 2 Oxetane ring proton coupling constants (Hz)

Oxetanes	$J_{3,4}$[a] J_{cis}	$J_{3,4}$[a] J_{trans}	$J_{3,3}$	Ref.
 **9**	8.5	6.5		12*b*
 **10**-X	8.5–8.6	5.6–5.7		9*a*,9*b*
 **11** *n* = 1, 2			11.5	11
 **12**-X			11.7	9*c*
 **13**	8.9	6.7	11.6	11
 **5**-X	8.9–9.2	5.8–6.2	11.7	This work

2.5–3.6 ppm. In the nine oxetanes we have studied, the oxetane ring proton absorptions fell in two distinct regions, 2.6–2.9 and 5.0–5.1 ppm (see Experimental section), which is in good agreement with the above description and our previous observations in other structural related oxetanes.[9] The magnitude of the geminal coupling (*ca*. 11.7 Hz) of the oxetane ring protons provides further evidence for the oxetane structures **5** (see Table 2). The other regioisomer **8** would have a geminal coupling $J_{\alpha,\alpha}$ of 6.0 as described by Lustig *et al.*[15a] for the oxetane ring C_α protons.

Another indication of structure **5** instead of **8** comes from ^{13}C NMR study, where the chemical shift difference (Δδ) between C-8 and C-10 and between C-4 and C-9 is similar and falls into the range of 0.2 ppm (see Table 3). However, previous studies[9b] show that a large difference in chemical shifts for carbons in proximity to the cyanomethylene group is expected (due to the magnetic anisotropy of the cyano group); *i.e.* if **8** had been formed, the chemical shift difference (Δδ) would have been larger than 0.5 ppm.

Although a single crystal X-ray structure determination would define the structural assignment, all our attempts to grow a single crystal of compounds **5**-X were unsuccessful. Fortunately, the configuration assignment of the spiro skeleton was found to be consistent with a ^{13}C NMR study of the type described by le Noble *et al.*[16] In essence, this is an additivity scheme in which the chemical shifts are calculated from those of the corresponding carbons in adamantane, 1-fluoroadamantane and the parent spirooxetane. The C-4,9 and C-8,10

Table 3 Calculated[a] and observed[b] ^{13}C chemical shifts in 5-substituted-4′-cyanospiro[adamantane-2,2′-oxetanes]

Carbon	**5**-H	*anti*-**5**-F	*syn*-**5**-F	*anti*-**5**-Cl	*syn*-**5**-Cl	*anti*-**5**-Br	*syn*-**5**-Br	*anti*-**5**-Ph	*syn*-**5**-Ph
C-1, C-3	38.87	40.59 (41.47) *J* 8.8[c]	41.35 (41.47) *J* 11.0	41.02 (41.47)	41.45 (41.47)	41.87	42.15	38.95	39.15
	38.57	40.73 (41.67) *J* 11.0[c]	41.50 (41.67) *J* 11.0	41.16 (41.67)	41.60 (41.67)	41.98	42.30	39.04	39.24
C-2	91.19	89.12 (89.30)	89.24 (89.30)	88.86 (88.80)	88.42 (88.80)	88.74	88.36	90.61	90.20
C-4, C-9	33.03	37.62 (37.94) *J* 19.8	36.30 (36.28)[d]	42.76 (42.64)	41.19 (41.04)[f]	44.28	42.65	38.48	36.91
	33.15	37.74 (38.06) *J* 19.8	36.59 (36.34)[d]	42.88 (42.76)	41.19 (40.98)[f]	44.40	42.71	38.65	37.14
C-5	26.04	90.58 (89.94) *J* 184.6	90.46 (89.96) *J* 184.6	65.23 (65.84)	65.35 (65.96)	61.44	61.70	34.90	34.64
C-7	26.16	29.16 (29.26) *J* 9.2	29.29 (29.14) *J* 11.0	29.39 (29.26)	29.42 (29.14)	30.21	30.18	26.80	26.89
C-6	36.24	41.61 (41.15) *J* 15.4	41.53 (41.15) *J* 15.4	46.44 (45.85)	46.35 (45.85)	47.89	47.83	42.30	41.63
C-8, C-10	31.37	29.92 (29.48)[e]	31.55 (31.14)	29.62 (29.98)	31.29 (30.64)	29.60	31.26	30.62	32.28
	31.43	29.92 (29.54)[e]	31.63 (31.26)	29.68 (29.04)	31.37 (30.76)	29.65	31.37	30.67	32.42
C-3′	37.23	36.97	35.92	37.03	36.12	37.03	36.27	37.32	36.91
C-4′	59.90	59.96	59.93	59.96	59.96	59.98	59.96	60.04	60.01
CN	119.74	119.34	119.39	119.31	119.37	119.31	119.34	119.69	119.71
C-*i*								149.06	149.49
C-*o*								124.73	124.78
C-*m*								128.28	128.16
C-*p*								126.01	125.83

[a] Calculated values are in parentheses. [b] Measured by a VXR-300 NMR spectrometer operated at 75.4 MHz and reported on the δ scale, $CDCl_3$ (77.00 δ). See Scheme 1 for the numbering system. In the parent compound **5**-H, the oxygen is understood to be *syn* to C-8 and C-10. [c] C-1 and C-3 were overlapped. [d] C-4 and C-9 were overlapped so the coupling constant *J* values were not determined. [e] Two peaks overlapped at δ 29.92. [f] Two peaks overlapped at δ 41.19.

pairs, by far the most informative beacons in this regard, are readily distinguished from one another by virtue of the ^{13}C–^{19}F splittings, which are *ca*. 20 and 0 Hz, respectively (Table 3). In the parent compound, they can be recognized by means of their chemical shifts: when one of the two substituents at C-2 is an electronegative atom such as oxygen, the carbon pair 'below' it is always shielded compared to the *anti* pair.[9] The chemical shifts thus computed for C-4,9 and C-8,10 agree with the observed values to within a few tenths of 1 ppm; differences of 1 ppm or more result if the opposite configurations are assumed (Table 3).

The experiments with **1**-Cl, -Br, -Ph and -OH followed a similar course; *i.e.* the *anti*:*syn* ratio is *ca*. 60:40 in all cases (Table 1). The *anti* and *syn* assignments in these instances were also based on the ^{13}C additivity method. As with the fluoro products, the chemical shifts calculated for C-4,9 and C-8,10 agree with the observed values to within a few tenths of 1 ppm (see Table 3). Furthermore, the ^{13}C chemical shifts can be more closely predicted to within 0.2 ppm using the additivity scheme from known oxetanes (**12**),[9c] which is much smaller compared to those calculated from adamantanes (≤0.65 ppm).[16]

Many of the adamantanone reactions have been interpreted by le Noble[3] and Cieplak[1] as consistent with the Cieplak hypothesis since the reaction occurs preferentially from the face antiperiplanar to the more electron-rich σ-bonds. Cieplak contends this is a result of the preferential donation from the more electron-rich bond to the σ*‡ orbital shown schematically in Fig. 1.[1,3] The present results add to the already extensive evidence for the proposition that addition to trigonal carbon occurs at the face antiperiplanar to electron-rich vicinal bond(s). It would seem difficult to find a reason for this preference in so many reactions as described here and elsewhere without involving transition-state hyperconjugation. A recent report by Coxon and Houk[2c] using *ab initio* and semiempirical methods to calculate the transition state energies of *syn* and *anti* face approaches of **1**-X by AlH_3 also concluded that hyperconjugative stabilization dominates the electronic effects. It must be realized, however, that our knowledge of inductive power is based almost exclusively on ground-state chemistry,

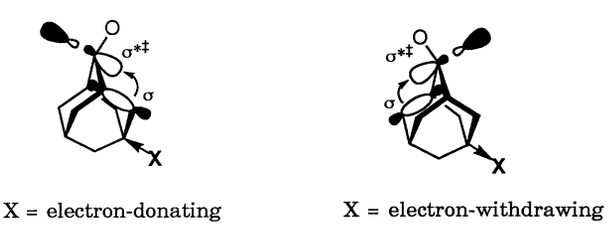


Fig. 1 Cieplak preference for nucleophilic (or electrophilic) addition *anti* to electron-donating (left) and *syn* to electron-withdrawing substituents (right)

and also that with the *E*/*Z* ratios generally rather close to unity, it will remain difficult to satisfactorily prove or disprove such a correlation in excited state chemistry.

Experimental

^{1}H NMR spectra were measured on 300 and 400 MHz spectrometers. The data reported were recorded at 300 MHz unless otherwise specified. Natural abundance ^{13}C NMR spectra were measured using pulsed Fourier-transform, on a Varian Unity-300 MHz, high resolution NMR spectrometer, operating at 75.4 MHz. Broad-band decoupling was used to simplify spectra and aid peak identification. δ values are in ppm and *J* values in Hz for both nuclei, with the solvent (usually $CDCl_3$) peak as an internal standard. The reference peak for ^{13}C is δ 77.00, which is set at the centre peak of $CDCl_3$, and for ^{1}H it is δ 7.25 of $CHCl_3$.

Gas chromatographic analyses were carried out on an instrument equipped with a flame ionization detector and a reporting integrator. The capillary column employed included HP-1 crosslinked methylsilicone (SE-30, 25 m) and Carbowax column (25 m). GC–MS analyses were carried out using EI (at 70 eV).

Materials

All commercially obtained chemicals were reagent or spectrophotometric grade and were not purified prior to use unless

otherwise specified. The synthesis of 5-fluoro-adamantan-2-ones (**1**-F),[17,18] 5-chloro- (**1**-Cl),[19] 5-bromo- (**1**-Br),[20] and 5-phenyladamantan-2-one (**1**-Ph),[18] have all been described. All the 5-substituted 2-methyleneadamantanes (**7**-Xs) were prepared from the corresponding ketones (**1**-X) by a standard procedure described by Adcock *et al.*[6a] for the bromo derivative (X = Br).

General procedure for the synthesis of 5-substituted 2-methyleneadamantane (7-X)

By use of a procedure similar to that described by Adcock,[6a] a solution of butyllithium (24 ml of 2.5 M hexane solution; 60 mmol) was added over a 10 min period to a stirred slurry of methyltriphenylphosphonium bromide (19.6 g, 55 mmol) in dry diethyl ether (100 ml) in a 250 ml twin-necked flask under N_2. The reaction mixture was stirred for 4 h at room temp. before adding dropwise a solution of adamantane-2-one **1**-H (7.51 g, 50 mmol) in dry diethyl ether (80 ml). The mixture was stirred overnight then 10 ml water was added and stirred for 10 min. The organic layer was separated and the aqueous layer was washed with diethyl ether (20 ml × 2). The combined extracts were washed with brine, dried over $MgSO_4$, and the solvent was removed *in vacuo* to afford a yellow oil. Chromatography over silica gel using hexane as eluent gave the desired compound **7**-H as a colourless solid (mp 135–136 °C; lit.,[6a] 135–136 °C) 5.28 g (72%): δ_H 4.50 (2 H, s), 2.48 (2 H, s) and 1.93–1.76 (12 H, m); δ_C 158.41 (C_q), 100.54 (CH_2), 39.65 (CH_2), 39.06 (CH), 37.29 (CH_2) and 28.28 (CH).

7-F was a colourless solid (mp 112–114 °C; lit.,[6a] 110–112 °C) 70%: δ_H 4.57 (2 H, s), 2.69 (2 H, br s), 2.26 (1 H, br s), 1.96–1.91 (6 H, m) and 1.70–1.69 (4 H, m); δ_C 154.02 (C_q), 103.40 (CH_2, d, *J* 2.5), 91.70 (C_q, d, *J* 184.3), 43.63 (CH_2, d, *J* 17.1), 42.41 (CH_2, d, *J* 17.1), 40.65 (CH, d, *J* 9.8), 37.92 (CH_2, d, *J* 2.5) and 31.47 (CH, d, *J* 9.8).

7-Cl was a colourless liquid 67%: δ_H 4.57 (2 H, s), 2.63 (2 H, s), 2.19–2.17 (7 H, m) and 1.80–1.67 (4 H, m); δ_C 153.63 (C_q), 103.31 (CH_2), 67.39 (C_q), 48.68 (CH_2), 47.25 (CH_2), 41.10 (CH), 37.46 (CH_2) and 31.31 (CH).

7-Br was a colourless liquid 70%: δ_H 4.56 (2 H, s), 2.61 (2 H, s), 2.42–2.39 (6 H, m), 2.14 (1 H, br s) and 1.86–1.73 (4 H, m); δ_C 157.57 (C_q), 103.51 (CH_2), 64.73 (C_q), 50.37 (CH_2), 48.54 (CH_2), 42.12 (CH), 37.46 (CH_2) and 32.38 (CH).

Irradiation of 1-X with 4

A relatively high concentration of **4** (1.7 M) was employed to favour the formation of oxetanes. Thus, a solution of 0.1 g of **1**-X and 2.18 ml of **4** in 20 ml of spectrograde acetonitrile was placed in a Pyrex tube stoppered with a rubber septum. The solution was irradiated at 300 nm in a Rayonet reactor for *ca.* 6–10 d (>98% conversion) until completion (checked by GC). The solvent was removed from the dark-red solution on a rotary evaporator and the residue was redissolved in ethyl acetate with sonication. The solution was filtered to remove undissolved solids, then concentrated on a rotary evaporator. The residues of all 5-substituted oxetanes were chromatographed over silica gel with ethyl acetate in hexanes (ethyl acetate : hexanes = 1 : 10; v : v) as eluent. The use of 40–63 μm silica gel 60 (E. Merck No 9385) and a pressure-driven rate of 1.0 in min^{-1} leads to a successful separation. In every instance, *anti*-**5**-X eluted first, followed by *syn*-**5**-X. *anti*- and *syn*-**5**-OH were not separable by either SiO_2 or aluminium oxide.

The peak patterns in the ^{1}H ($CDCl_3$, 300 MHz) and ^{13}C NMR spectra for all the oxetanes are very similar (for complete assignments of the ^{13}C peaks see Table 2).

4′-Cyano-spiro[adamantane-2,2′-oxetane] (5-H). A colourless solid (mp 59 °C), δ_H($CDCl_3$, 300 MHz): 5.07–5.01 (1 H, dd, *J* 5.79, 8.86), 2.83–2.76 (1 H, dd, *J* 8.86, 11.72), 2.70–2.64 (1 H, dd, *J* 5.79, 11.72), 2.36 (1 H, br s), 2.08–1.92 (4 H, m) and 1.81–1.54 (9 H, m); MS (EI) *m*/*z* 203 (M^+, 4%), 150 ($M^+ -$ **4**, 100), 148 [$M^+ -$ O=C(CN)H, 24], 91 (34) and 79 (56). HRMS (*m*/*z*). Calc. for $C_{13}H_{17}NO$: 203.1310. Found: 203.1309.

***anti*-4′-Cyano-5-fluoro-spiro[adamantane-2,2′-oxetane] (*anti*-5-F).** A colourless solid (mp 85–86 °C), δ_H 5.05–5.00 (1 H, dd, *J* 6.08, 8.82), 2.86–2.79 (1 H, dd, *J* 8.82, 11.72), 2.73–2.67 (1 H, dd, *J* 6.08, 11.72), 2.55 (1 H, br s), 2.28 (1 H, br s), 2.16 (1 H, br s) and 2.15–1.79 (10 H, m); MS (EI) *m*/*z* 221 (M^+, 6%), 168 ($M^+ -$ **4**, 100), 166 [$M^+ -$ O=C(CN)H, 9] and 97 (36). HRMS (*m*/*z*). Calc. for $C_{13}H_{16}FNO$: 221.1216. Found: 221.1205.

***syn*-4′-Cyano-5-fluoro-spiro[adamantane-2,2′-oxetane] (*syn*-5-F).** A colourless solid (mp 78–79 °C), δ_H 5.06–5.01 (1 H, dd, *J* 6.01, 8.89), 2.84–2.77 (1 H, dd, *J* 8.89, 11.72), 2.70–2.64 (1 H, dd, *J* 6.01, 11.72), 2.62 (1 H, br s), 2.34 (1 H, br s), 2.23–2.10 (3 H, m), 1.85 (2 H, br s) and 1.74–1.50 (6 H, m); MS (EI) *m*/*z* 221 (M^+, 19%), 168 ($M^+ -$ **4**, 100), 166 [$M^+ -$ O=C(CN)H, 69], 97 (51) and 79 (22). HRMS (*m*/*z*). Calc. for $C_{13}H_{16}FNO$: 221.1216. Found: 221.1219.

***anti*-4′-Cyano-5-chloro-spiro[adamantane-2,2′-oxetane] (*anti*-5-Cl).** A colourless solid (mp 97–98 °C), δ_H 5.05–5.00 (1 H, dd, *J* 5.75, 9.15), 2.86–2.79 (1 H, dd, *J* 9.15, 11.72), 2.73–2.67 (1 H, dd, *J* 5.75, 11.72), 2.21 (1 H, br s), 2.17–1.91 (9 H, m) and 1.87–1.23 (3 H, m); MS (EI) *m*/*z* 237 (M^+, 2%), 202, ($M^+ -$ Cl, 1), 184 ($M^+ -$ **4**, 100), 182 [$M^+ -$ O=C(CN)H, 2], 91 (17) and 79 (17). HRMS (*m*/*z*). Calc. for $C_{13}H_{16}ClNO$: 237.0920. Found: 237.0915.

***syn*-4′-Cyano-5-chloro-spiro[adamantane-2,2′-oxetane] (*syn*-5-Cl).** A colourless liquid, δ_H 5.06–5.01 (1 H, dd, *J* 6.00, 8.88), 2.82–2.76 (1 H, dd, *J* 8.88, 11.72), 2.69–2.63 (1 H, dd, *J* 6.00, 11.72), 2.62 (1 H, br s), 2.54–2.31 (3 H, m), 2.23–2.15 (3 H, m), 2.03–1.87 (3 H, m) and 1.74–1.23 (3 H, m); MS (EI) *m*/*z* 237 (M^+, 3%), 202, ($M^+ -$ Cl, 7), 184 ($M^+ -$ **4**, 100), 182 [$M^+ -$ O=C(CN)H, 6], 91 (18) and 79 (16). HRMS (*m*/*z*). Calc. for $C_{13}H_{16}ClNO$: 237.0920. Found: 237.0922.

***anti*-4′-Cyano-5-bromo-spiro[adamantane-2,2′-oxetane] (*anti*-5-Br).** A colourless solid (mp 117–118 °C), δ_H 5.50–5.00 (1 H, dd, *J* 6.16, 9.23), 2.88–2.81 (1 H, dd, *J* 9.23, 11.72), 2.74–2.68 (1 H, dd, *J* 6.16, 11.72), 2.31 (1 H, br s), 2.31–2.18 (9 H, m) and 2.07–1.93 (3 H, m); MS (EI) *m*/*z* 283 [$(M + 2)^+$, 0.1%], 281 (M^+, 0.1), 230 [$(M + 2)^+ -$ **4**, 1], 228 ($M^+ -$ **4**, 1), 202 ($M^+ -$ Br, 100), 146 (76), 91 (50) and 79 (44). HRMS (*m*/*z*). Calc. for $C_{13}H_{16}{}^{79}BrNO$: 281.0415. Found: 281.0422.

***syn*-4′-Cyano-5-bromo-spiro[adamantan-2,2′-oxetane] (*syn*-5-Br).** A colourless liquid, δ_H 5.06–5.01 (1 H, dd, *J* 6.00, 8.89), 2.81–2.74 (1 H, dd, *J* 8.89, 11.72), 2.67–2.62 (1 H, dd, *J* 6.00, 11.72), 2.56–2.50 (2 H, m), 2.29 (2 H, br s), 2.23–2.09 (3 H, m), 1.99 (1 H, br s) and 1.97–1.58 (5 H, m); HRMS (*m*/*z*). Calc. for $C_{13}H_{16}{}^{79}BrNO$: 281.0415. Found: 281.0425.

***anti*-4′-Cyano-5-phenyl-spiro[adamantane-2,2′-oxetane] (*anti*-5-Ph).** A colourless solid (mp 107–108 °C), δ_H 7.35–7.17 (5 H, m), 5.10–5.05 (1 H, dd, *J* 6.07, 8.82), 2.88–2.81 (1 H, dd, *J* 8.82, 11.72), 2.75–2.69 (1 H, dd, *J* 6.07, 11.72), 2.53 (1 H, br s), 2.25 (1 H, br s) and 2.13–1.56 (10 H, m); MS (EI) *m*/*z* 279 (M^+, 48%), 226 ($M^+ -$ **4**, 100), 224 [$M^+ -$ O=C(CN)H, 5], 168 (27), 155 (53) and 91 (24). HRMS (*m*/*z*). Calc. for $C_{19}H_{21}NO$: 279.1623. Found: 279.1614.

***syn*-4′-Cyano-5-phenyl-spiro[adamantane-2,2′-oxetane] (*syn*-5-Ph).** A colourless solid (mp 103–104 °C), δ_H 7.36–7.17 (5 H, m), 5.10–5.05 (1 H, dd, *J* 5.73, 9.16), 2.90–2.83 (1 H, dd, *J* 9.16, 11.72), 2.78–2.72 (1 H, dd, *J* 5.73, 11.72), 2.55 (1 H, br s) and 2.33–1.64 (12 H, m); MS (EI) *m*/*z* 280 [$(M + 1)^+$, 21%), 279 (M^+, 100%), 226 $M^+ -$ **4**, 100), 224 [$M^+ -$ O=C(CN)H, 7], 209 (20), 168 (24), 155 (58) and 91 (30). HRMS (*m*/*z*). Calc. for $C_{19}H_{21}NO$: 279.1623. Found: 279.1619.

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