Facial selectivity in the addition of nucleophiles to the radical cations of substituted 2-methyleneadamantanes

Susan Swansburg, Kristin Janz, Gloria Jocys, Alexandra Pincock, and James Pincock

Abstract: The diphenylmethylenecyclohexane, **2**, and the substituted 2-methyleneadamantanes, **3**–**7**, have been prepared. The radical cation of each was generated by photochemical oxidation using 1,4-dicyanobenzene as the sensitizer, and their reactivity was examined in methanol–acetonitrile mixtures with added tetraethylammonium cyanide. Although compound **2** reacted only by tautomerization, the other compounds all gave addition products. For the monoaryl alkenes **3**, **4,** and **5**, comparable yields of both methanol and HCN addition products were obtained, resulting from nucleophilic attack at either end of the alkene radical cation. For the diphenylalkenes **6** and **7**, the regioselectivity favored nucleophilic attack at the adamantyl carbon, and the addition products were predominantly those of HCN addition. For the 5-methoxy compound **7**, HCN addition was facially selective with a *syn:anti* ratio of 58:42.

Key words: methyleneadamantanes, facial selectivity, radical cations.

Résumé : On a préparé le diphénylméthylènecyclohexane, **2**, ainsi que les 2-méthylèneadamantanes substitués **3**–**7**. On en a ensuite préparé les cations radicaux par une oxydation photochimique impliquant le 1,4-dicyanobenzène comme sensibilisateur et on a étudié leur réactivité dans des mélanges de méthanol–acétonitrile dans lesquels on a ajouté du cyanure de tétraméthylammonium. Même si le composé **2** ne réagit que par tautomérisation, tous les autres composés conduisent à des produits d'addition. Pour les monoarylalcènes **3**, **4** et **5**, on a obtenu des rendements comparables de produits d'addition de méthanol et de HCN provenant d'une attaque nucléophile à l'une des deux extrémités du cation radical de l'alcène. Pour les diphénylalcènes **6** et **7**, la régiosélectivité favorise l'attaque nucléophile sur le carbone adamantyle; les produits d'addition proviennent alors en prédominance d'une addition de HCN. Pour le composé 5-méthoxy **7**, l'addition du HCN se fait sélectivement sur une face et le rapport *syn : anti* est égal à 58 : 42.

Mots clés : méthylèneadamantanes, sélectivité faciale, cations radicaux.

[Traduit par la rédaction]

Introduction

The factors that control diastereoselectivity in additions to planar carbon atoms continue to attract considerable experimental (1–4) and theoretical (5) interest. In a pioneering study (6), le Noble and co-workers showed that substituted 5-X-2-adamantyl systems,[2] **1**, are particularly useful probes in these studies. Steric differences between the *syn* and *anti*[3] faces are minimized, there is none of the conformational ambiguity inherent in more flexible systems, and only two products can be formed. Therefore, the long-range electronic effect between the substituent and the reaction center at C2 can be assessed by the ratio of *syn* to *anti* products. With very few exceptions, *syn* attack is preferred. Because most of the X groups studied have been inductively electron withdrawing (relative to H at C7), *syn* represents attack on the same side as the electron-deficient σ bonds (C1—C9 and C3—C4) but antiperiplanar to the electron-rich σ bonds (C1—C8 and C3—C10). Current debate focuses mainly on whether the observed diastereoselectivities are controlled by hyperconjugative or electrostatic field effects.

Examples of the types of reactions that have been studied include nucleophilic additions to 2-adamantanones (1, 3), electrophilic additions to 2-methyleneadamantenes (3), solvolysis of 2-adamantyl compounds (6–8), radical trapping

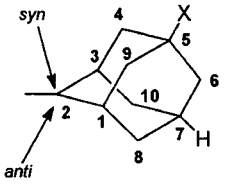
Received July 30, 1997.

S. Swansburg, K. Janz, G. Jocys, A. Pincock, and J. Pincock.[1] Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3, Canada.

[1] Author to whom correspondence may be addressed. Telephone: (902) 494-3324. Fax: (902) 494-1310. E-mail: pincock@chem1.chem.dal.ca

[2] These numbers, depending on substituents, may or may not correspond to IUPAC numbering. They have been adopted by chemists studying the effect of substituents in adamantyl chemistry so that C2 is the site of interest and C5 is the position of the substituent.

[3] A variety of stereochemical designations have been used: *syn* = *zu* and *anti* = *en*. In reactions such as hydride or organometallic addition to 5-X-2-adamantanones, the carbonyl oxygen that becomes the alcohol of the product takes stereochemical nomenclature priority. Therefore, *syn* hydride reduction gives the *anti* or *E* product and *anti* attack gives the *syn* or *Z* product.



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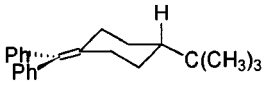

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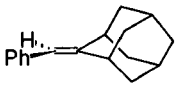

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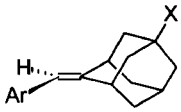
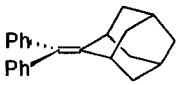


4: Ar = Anisyl, X = H

5: Ar = Ph; X = 4-OCH_3



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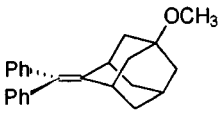
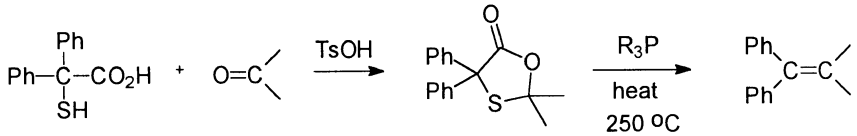


7

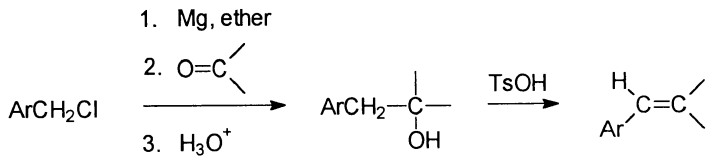
(9), sigmatropic rearrangements (Claisen) (10), and photochemical [2 + 2] cycloadditions of alkenes to 2-adamantanones (11, 12). Facial selectivity in the reactions of 5-aza (13), 5-azoxy (14), and perfluoro (15) adamantane derivatives have also been reported. To our knowledge, the reactivity of radical ions has not been studied. We now report on the syntheses of the derivatives **2**–**7** and the products obtained from their radical cations. These cations were generated by photochemical electron transfer using 1,4-dicyanobenzene (DCB) as the electron acceptor; the cations were then trapped by nucleophiles (methanol, cyanide ion) according to the well-established procedures developed by Arnold and Maroulis (16). The choice of substrates was made on the basis that aryl-substituted alkenes are readily oxidized by the excited singlet state of DCB, and that **5** and **7**, containing the 5-methoxy group, can both be prepared from commercially available 5-hydroxy-2-adamantanone.

[1]



2a, 6a, 7a

[2]



3a, 4a, 5a

Results and discussion

Syntheses of diphenyl alkenes 2, 6, and 7

The diphenylalkenes were synthesized from the corresponding 1,3-oxathiolan-5-ones **2a, 6a**, and **7a**, eq. [1], by pyrolysis at 250°C, in the presence of tris(diethylamino)phosphine. This twofold extrusion process, developed by Barton and Willis (17), provides a convenient route to these highly hindered alkenes. The 1,3-oxathiolan-5-ones were prepared by condensation of the appropriate ketone with thiobenzilic acid (*p*-toluenesulfonic acid catalysis) in benzene with azeotropic removal of water. For **2a** and **7a,** a mixture of diastereomers resulted; the ratio for both cases was close to 60:40. Separation of these isomers was possible by column chromatography but no attempt was made to assign the individual structures for **2a**. For **7a**, in the major isomer the sulfur was *syn* to the 5-methoxy group as determined by X-ray crystallography (Fig. 1).[4] We do not know if this represents a kinetic preference. Separation of the mixtures of **2a** and **7a** was not necessary for the next step as the stereochemical distinction is lost in the conversion to the alkene.

Syntheses of monophenyl alkenes 3, 4, and 5

Grignard reaction of 2-adamantanone or 5-methoxy-2-adamatanone with either benzyl chloride or 4-methoxybenzyl chloride gave alcohol products **3a**, **4a,** and **5a,** which were dehydrated in benzene (*p*-toluenesulfonic acid catalysis),

[4] T.S. Cameron and W. Kwiatkowski. Department of Chemistry, Dalhousie University, unpublished results, 1996.

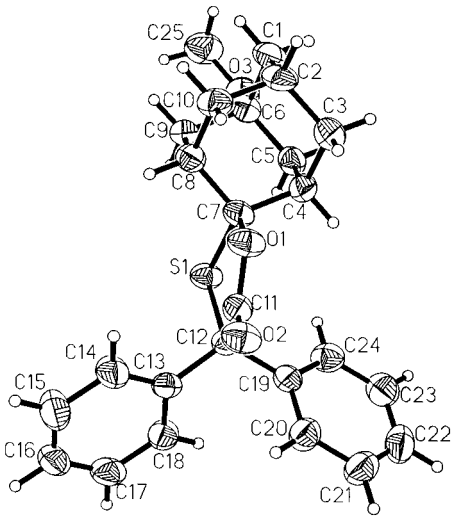
eq. [2]. The alcohol **3a** has been prepared previously by the same procedure but was converted to **3** by dehydration using phosphoric acid (18).

Photochemistry of 2

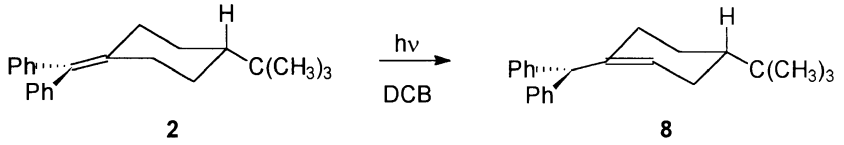
Although alkene **2** was prepared primarily to develop the synthetic and photochemical methodology required for the adamantyl systems, the reactivity of its radical cation is also of interest. The presence of the *tert*-butyl group at C4 locks the cyclohexane ring in a fixed conformation, making the approach of a nucleophile to the two faces of the carbon–carbon double bond very different for steric reasons. However, irradiation of alkene **2** with DCB as the sensitizer, in 3:1 acetonitrile:methanol, did not result in the formation of nucleophile addition products. Rather, the sole product observed was the tautomer of the starting material, **8** (eq. [3]), in which the carbon–carbon double bond is now endocyclic. In retrospect, this deconjugation reaction is not unexpected. Arnold and Mines (19) have reported several examples of photochemical tautomerization of alkenes, including diphenylmethylenecyclohexane, analogous to **2** but without the *tert*-butyl group. In their studies, 2,6-lutidine was added to facilitate the isomerization reaction but for alkene **2** no base was required.

The mechanism proposed (19) for these tautomerizations begins with photoinduced electron transfer to form the alkene radical cation (and the radical anion of DCB), followed by deprotonation at the allylic position. The acidity of these hydrogens is known to be enhanced in the radical cation. Reduction of the allylic radical by the radical anion of DCB gives the allylic anion, which on reprotonation by methanol results in either the starting alkene or its tautomer. The position of the equilibrium between the two isomers is controlled by their relative oxidation potentials. Between **2** and **8**, **2** has a considerably lower oxidation potential and is therefore photochemically converted to **8**, whereas **8**, with the higher oxidation potential, is not converted back to **2**. The efficiency of this conversion for **2**, relative to that of the other alkenes studied previously (19), is probably a result of the fact that the axial allylic carbon–hydrogen bond is fixed in an appropriate geometry for effective overlap with the singly occupied molecular orbital (SOMO) of the initially formed radical cation. Therefore, tautomerization occurs in preference to addition of methanol across the double bond. Even in the presence of

Fig. 1. ORTEP representation from the X-ray crystal structure of **7a**, isomer 1.

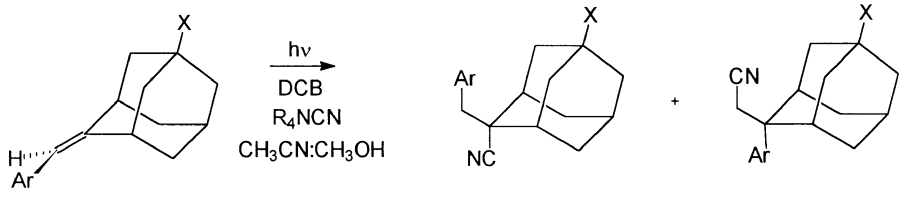


[3]



2 **8**

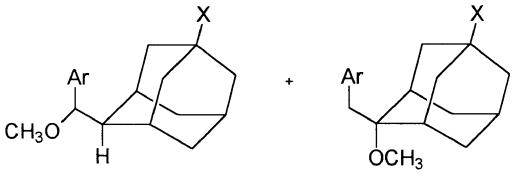
[4]



3: Ar = Ph; X = H
4: Ar = Anisyl; X = H

9: Ar = Ph; X = H
13: Ar = Anisyl; X = H

10: Ar = Ph; X = H
14: Ar = Anisyl; X = H



11: Ar = Ph; X = H
15: Ar = Anisyl; X = H

12: Ar = Ph; X = H
16: Ar = Anisyl; X = H

Fig. 2. ORTEP representation from the X-ray crystal structure of **9**.

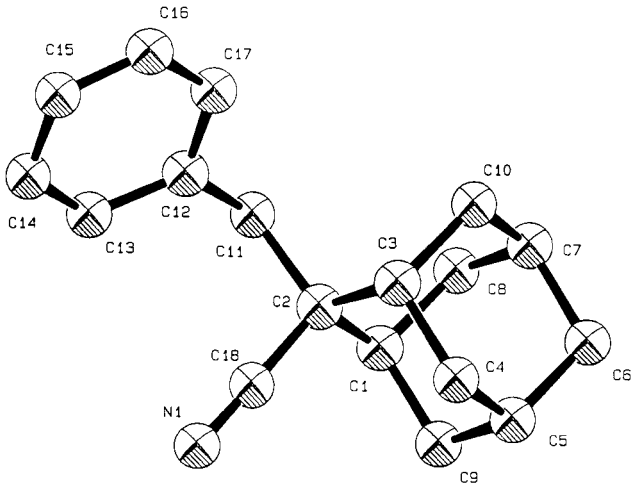
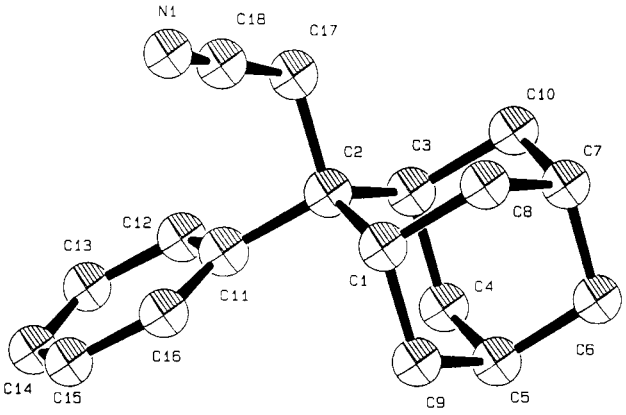


Fig. 3. ORTEP representation from the X-ray crystal structure of **10**.



tetraethylammonium cyanide, addition products were not formed in detectable yield; again, only **8** was observed.

Photochemistry of 3

In the adamantyl analogues, the tautomerization reaction is unlikely, because of the high strain associated with placing double bonds in adamantane rings (thermodynamic rationale) and also because the allylic hydrogens are not oriented appropriately for favourable overlap with the SOMO of the radical cation (kinetic rationale).

Irradiation of alkene **3** with DCB and added tetraethylammonium cyanide (4.5 mM) in 9:1 (by volume) acetonitrile:methanol gave the four addition products shown in eq. [4]. These products were identified, in a preliminary way, by their mass spectra (GC–MS). In all cases, the spectra are simple, showing a few prominent ions that are easily assigned to fragments of the molecules. For instance, the base peaks have *m/z* values corresponding to the following fragments: **9** (91, $PhCH_2$+), **10** (211, 2-Ph-Ad^+), **11** (121, $PhCH\text{-}OCH_3$+), **12** (225, 2-CH_3O-Ad^+). The four products were separated by preparative-scale column chromatography on silica gel. Detailed ^1H and ^{13}C NMR spectral analyses support the proposed structures. In addition, the structures of the HCN addition products, **9** and **10**, were confirmed by X-ray crystallography (Figs. 2 and 3).[4] The cyano group is directly bonded to C2 of the adamantane ring in **9**, but is on the exocyclic carbon in **10**. In the latter structure, the phenyl group has migrated to the adamantyl carbon, C2. Ether **11** was not isolated from the reaction mixture but a synthetic sample was prepared by hydroboration of alkene **3** followed by conversion to the methyl ether by treatment with sodium hydride and methyl iodide. Integration of the ^1H NMR signals of the crude reaction mixture for the hydrogens α to the phenyl ring indicated that **11/12** are formed in a ratio of one to three.

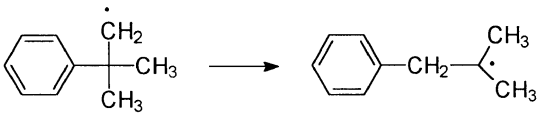
The yields for the reaction of **3**, by calibrated GC–FID analysis (corrected for unreacted starting material at 50% conversion of **3**), are as follows: **9** (34%), **10** (24%), **11** plus **12** (25%); the mass balance is 81%. The yield of the two products resulting from addition of cyanide ion is greater than that of those resulting from addition of methanol, as expected based on the relative reactivities of the two nucleophiles. Johnston and Schepp (20, 21) have measured second-order rate constants for the addition of nucleophiles to a series of substituted styrene radical cations generated directly from the parent alkene by laser flash photolysis. For each radical cation studied, the rate constant for methanol addition was orders of magnitude slower than for any other nucleophile studied. For instance, the rate constant for reaction of the 4-methoxystyrene radical cation in 4:1 water:acetonitrile is 3×10^4 M^{-1} s^{-1} for methanol and 1.0×10^8 M^{-1} s^{-1} for cyanide ion.

The established mechanism for these addition reactions involves product-determining attack of the nucleophile on the radical cation. To confirm that the radical cation of **3** is formed efficiently, the quenching of DCB fluorescence by **3** was examined. The Stern–Volmer slope gave $k_q\tau_{DCB} = 17$ M^{-1}. Using 9.7 ns as the singlet lifetime of DCB (16), the calculated quenching rate constant is 1.8×10^{10} M^{-1} s^{-1}, comparable to the diffusional limits (22) in acetonitrile (1.9×10^{10} M^{-1} s^{-1}) and methanol (1.2×10^{10} M^{-1} s^{-1}), suggesting that formation of the radical cation will occur readily. As predicted by the Weller equation (23), oxidation of **3** by the excited singlet state of DCB should be exothermic if the oxidation potential of the alkene is below 2.2 V; the measured value for **3** is 1.37 V (CH_3CN versus SCE).

The cyano adducts **9** and **10** are formed in a ratio of 1.4:1, invariant with percent conversion. This ratio is, at least in part, a reflection of the relative stabilities of the benzyl and tertiary radicals formed by attack of cyanide ion at the two ends of the double bond of the radical cation of **3**. For addition to diphenylethylene, the nucleophile adds exclusively to the radical cation at the terminal carbon to give the more stable diphenylmethyl radical intermediate. Therefore, the result is anti-Markovnikov addition (16). For **3**, the two possible radical intermediates are of comparable stability. The benzylic radical is formed in slight preference to the tertiary one, and **9** is therefore the expected product. Cyanide ion attacks the radical cation at the 2-adamantyl position, and this is followed by reduction (by the radical anion of DCB) of the radical to the anion, and subsequent protonation of the anion by the solvent, methanol. In contrast, product **10** was unexpected. The phenyl group has migrated to C2 of the adamantane ring. A reasonable pathway for formation of this product requires several steps: attack of the cyanide ion on the radical cation to form the tertiary 2-adamantyl radical, 1,2-migration of the phenyl group to give the α-cyano radical, reduction of this radical to the

corresponding anion, and finally protonation of the anion by the solvent.

Several facts support this mechanism. First, the tertiary radical would be relatively long-lived. Oxidation potentials indicate that it will not be reduced by the radical anion of DCB, because the oxidation potential of the radical anion of DCB (1.6 V) (24) is lower than that of the *tert*-butyl anion (greater than 2.0 V) (25). Second, although radical rearrangements are uncommon, examples of 1,2-phenyl migrations are well known (26). For instance, this so-called neophyl rearrangement for the 2-phenyl-2-methylpropyl radical is shown in eq. [5]; Franz et al. (27) determined the rate constant for this 1,2-phenyl migration to be 764 s^{-1} at 298 K. A similar 1,2-phenyl shift can be proposed in the formation of **10**. Although the rearrangement should be slower, since the precursor radical

[5] 

is tertiary, the low concentration of the radical would allow this relatively slow unimolecular process to compete with bimolecular processes. Third, once formed, the α-cyano radical would be easily reduced to the corresponding cyano-stabilized anion. None of the possible product resulting from trapping of the initially formed tertiary radical in this sequence was detected.

Similar 1,2-phenyl migrations have been observed for the radical cation induced epoxidation of both **3** (28) and **6** (28, 29) but the rearrangements proceed by a secondary reaction of the radical cation of the first formed epoxide.

Another mechanism for cyanide addition to **3** is possible. As mentioned above, the reactions of the radical cations of a variety of substituted styrenes with nucleophiles have been studied by laser flash photolysis (20, 21). In some cases, the mechanism has been shown to involve initial electron transfer to regenerate the original alkene along with the oxidized nucleophile. Combination of these two species could give the same radical as is formed in the above mechanism. However, this possibility can probably be excluded. It was not observed in the laser flash experiments with cyanide ion as the nucleophile. Moreover, for this pathway to be efficient, the oxidation potential of **3** (1.37 V, CH_3CN versus SCE) must be higher than that of cyanide ion. The latter oxidation potential is quite solvent dependent (30), with a value of 1.3 V in acetonitrile and 1.7 V in the protic solvent, water. Because of the methanol used in the 9:1 acetonitrile:methanol medium in these photolysis reactions, the oxidation potential of cyanide ion is likely to be closer to the value for water. Therefore, reaction by electron transfer of the radical cation of **3** with cyanide ion is probably endergonic, making this second mechanistic possibility unlikely.

The two ether products, **11** and **12**, were not separated by GC and were therefore quantified together. As mentioned above, they were formed in a ratio of one to three as determined by ^{1}H NMR integration. These ethers are the two regioisomers resulting from reaction of methanol with either end of the carbon–carbon double bond of the radical cation of **3**. Again, addition favours formation of the benzylic radical over the tertiary one although the degree of selectivity differs somewhat for the two nucleophiles. Methanol (3:1) is more selective than cyanide ion (1.4:1). There is still no firm mechanistic rationale for the regioselectivity of methanol addition to the radical cations of phenyl-substituted alkenes (31). In the current proposals, methanol initially adds to the radical cation to give a distonic radical cation and this addition may proceed through an encounter complex. Until the two possible distonic radicals are deprotonated to give radicals, this addition process may be reversible. The observed regiochemistry may then result, in a complex way, from a combination of both the rates of formation and the thermodynamic stability of these intermediates.

A product analogous to **10**, resulting from migration of the phenyl group, was not detected in the methanol addition products. One possible explanation is that a methoxy substituent should not stabilize a radical centre to as great an extent as would a cyano substituent (32). Therefore, the neophyl rearrangement may not be energetically favorable.

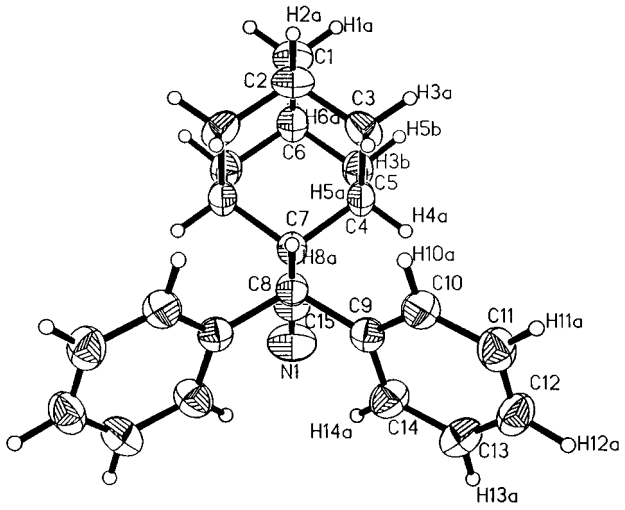
As in the cyano case, the tertiary radical intermediate from methanol addition is not reduced by the radical anion of DCB. Therefore, ether **11** probably results from hydrogen abstraction by this radical rather than from protonation of the corresponding anion. To test this conclusion, the photoreaction was repeated using CH_3OD in the presence of added cyanide ion in 9:1 acetonitrile:methanol. The amount of deuterium incorporated into each of the four products was determined from single ion monitoring mass spectrometry (SIMS), using the intensities of the M, M + 1, and M + 2 peaks. As expected from the above mechanistic proposal, both cyano adducts, **9** and **10**, contained deuterium in 90% excess relative to natural abundance samples. The molecular ion of ether **12** was not intense enough to give reliable results, as it readily fragmented in the mass spectrometer, with the base peak corresponding to the 2-methoxy-2-adamantyl cation. However, SIMS analysis of the C_7H_7 fragment ions at *m*/*z* 91, 92, and 93 gave only 30% of deuterium in excess of natural abundance. This result must be interpreted with caution, as more than one mass spectral fragmentation pathway may lead to ions at these masses. However, the enhanced percentage of deuterium found for this fragment ion suggests that, at least part of the time, the precursor radical to **12** is reduced and protonated by the solvent. Ether **11** showed only 5% deuterium in excess of natural abundance, which is consistent with hydrogen atom abstraction as the major pathway from tertiary radical to product.

Photochemistry of 4 and 5

Because the product mixtures obtained from **3** were fairly complex, alkene **4** was also studied, with the hope that the added 4-methoxy group would improve the regioselectivity of the attack at C2 of the adamantane ring.

Photoreaction of alkene **4**, under the same conditions as used for **3**, gave the products **13**–**16**, also shown in eq. [4]. The ratio of (**13** + **14**) to (**15** + **16**) was 3.8:1. These products are structurally parallel to those formed upon reaction of alkene **3**, but the relative yields are quite different. The yield of cyano adduct **14**, involving migration of a phenyl group, was extremely low; integration of the ^{1}H NMR signals for the methylene protons suggested a ratio for **13**/**14** of approximately 10:1. In fact, **14** was detected mainly because its presence was expected based on the products from the reaction of **3**.

Fig. 4. ORTEP representation from the X-ray crystal structure of **17**.



As was the case with **3**, an HCN addition product derived from the unrearranged tertiary radical intermediate was not detected. These results demonstrate that cyanide ion addition to the radical cation of **4** is highly regioselective. Presumably, the presence of a 4-methoxy substituent on the phenyl ring stabilizes the benzyl radical, favouring its formation relative to the unsubstituted case. As with alkene **3**, the regioselectivity of addition is much less pronounced when methanol is the nucleophile as compared to cyanide ion. Integration of characteristic ^{1}H NMR signals from a spectrum of the product mixture gave a ratio of the ether products, **15:16**, equal to 1.5:1.

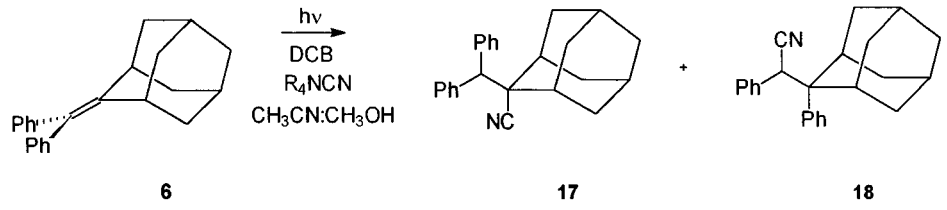
Some initial experiments towards studying facial selectivity in reactions of **5** were undertaken. The alkene was prepared, in low yield, but the product mixtures obtained in the photochemistry were complex and separations were difficult. These experiments were abandoned when the photochemistry of **6** indicated that **7** would be an easier probe to use than **5**.

Photochemistry of 6

Photolysis of **6** in 9:1 CH_3CN:CH_3OH with 9.8 mM tetraethylammonium cyanide gave one major product, **17**, and a minor one, **18**, eq. [6]. The ratio, by GC integration, was greater than 20:1. The structure of **17** was unambiguously established by X-ray crystallography, Fig. 4.[4] The minor product was not isolated and its structure was assigned only on the basis of its fragmentation in the GC–MS, where the base peak (*m/z*, 211) agreed with expected fragmentation of **18** to the 2-phenyl-2-adamantyl cation. The base peak for **17** (*m/z*, 177) corresponded to the diphenylmethyl cation. Evidence for low yields of methanol addition products was obtained by GC–MS, but these were not isolated either. By calibrated GC–FID analysis, a 61% yield of **17** was obtained after 85% conversion of **5**. These experiments show that the photochemistry of **5** is simpler than that of **3**. First, the regioselectivity of the addition reaction now greatly favors cyanide attack at the adamantyl tertiary carbon to give the diphenylmethyl radical. Second, the radical cation of the diphenyl alkene **6** is much more selective in its reaction with nucleophiles, cyanide ion reacting in preference to methanol. This is probably a result of its greater stability relative to the other radical cations studied and its consequent lower reactivity.

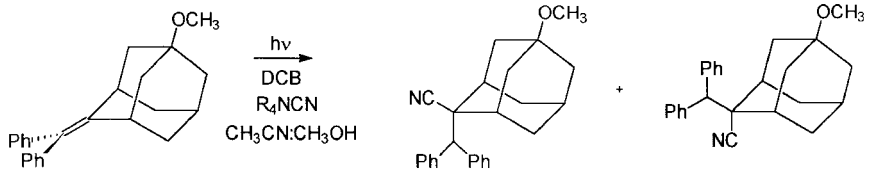
To confirm that photoinduced electron transfer was also efficient for this diphenyl derivative, fluorescence quenching experiments were again conducted. Stern–Volmer plots of the quenching of both DCB and 1,4-dicyanonaphthalene (DCN) by **6** were linear and gave $k_{eq}\tau$ values of 120 M^{-1} and 66 M^{-1}, respectively. Using the singlet lifetimes of 9.7 ns for DCB (16) and 10.1 ns for DCN (33) gives quenching rate constants of 1.3×10^{10} M^{-1} s^{-1} and 0.66×10^{10} M^{-1} s^{-1}, both values close to the diffusional limit, in agreement with expectations based on the Weller (23) equation and the oxidation potential of **6**,

[6]



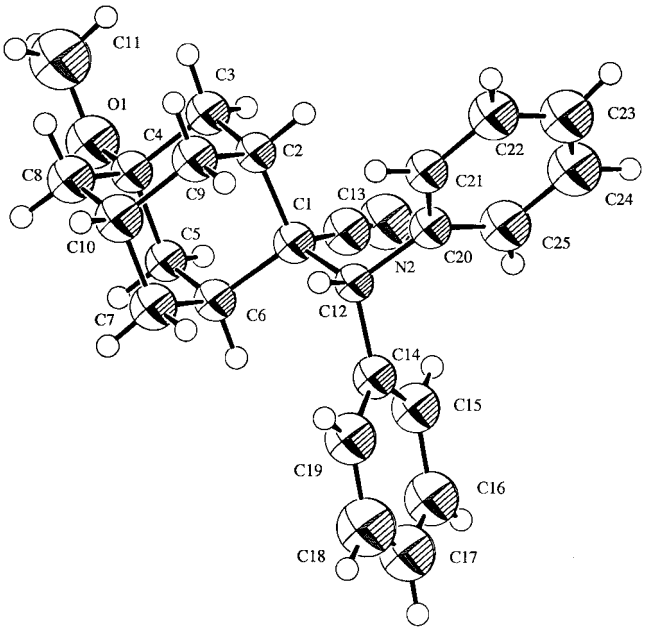
6 **17** **18**

[7]



7 **19** (51%) **20** (37%) **21** (12%)

Fig. 5. ORTEP representation from the X-ray crystal structure of **19**.



1.58 V (CH_3CN, vs. SCE); a value of 1.56 V (CH_2Cl_2, vs. SCE) has been reported (29).

Photochemistry of 7

The above results for the alkenes **2**–**6** suggested that the 5-methoxy substituted diphenyl derivative, **7**, would be the best choice for studying the facial selectivity of addition to these radical cations. In the presence of cyanide ion, irradiation of **6** gives only one major product; with the added methoxy substituent in **7**, the two major products should be the diastereomers resulting from nucleophilic attack at the two faces, and analysis of their ratio should be simple.

This assumption proved to be correct. Photolysis of **7** (240 mg) in 9:1 CH_3CN:CH_3OH with 4.6 mM tetraethylammonium cyanide resulted in over 90% conversion in only 2 h. The products formed, with yields by calibrated GC–FID at 78% conversion of **7**, are shown in eq. [7]; mass balance for these three products is 81%. The gross structures of the two major products, **19** and **20**, were again easily assigned by GC–MS since the base peak in both at *m/z* 167 corresponded to the diphenylmethyl cation; the minor isomer, **21**, resulting from migration of phenyl group by the same mechanism as for the other adamantane derivatives, had a base peak at *m*/*z* 241 corresponding to the 5-methoxy–2-phenyladamantyl cation.

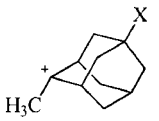
Pure samples of **19** and **20** were obtained by column chromatography and recrystallization. An X-ray structure for **19**, Fig. 5,[4] unambiguously assigns it to the *syn* isomer. This same assignment had been tentatively made by ^{13}C NMR spectra using both the chemical shifts for the unsubstituted HCN addition product, **17**, and the expected chemical shift effect of the added 5-methoxy group (34). The observed (calculated) δ values for the two compounds are, for **19**: C1,C3, 34.4 (34.2); C4,C9, 29.9 (29.8); C5, 28.6 (28.8); C6, 41.8 (41.6); C7, 70.5 (70.0); C8,C10, 38.2 (38.5) and for **20**: C1,C3, 34.9 (34.2); C4,C9, 35.1 (34.3); C5, 70.7 (70.0); C6, 40.7 (41.6); C7, 28.8 (28.8); C8, C10, 34.1 (34.1). The excellent agreement obtained is in accord with the assignments of the stereochemistry of **19** (and hence **20**) demonstrated by the crystal structure.

The ratio of the *syn* to *anti* isomers was obtained both by GC–FID (58:42) and by integration of the methoxy signals in the ^1H NMR spectrum (58:42) of the crude photolysis mixture. This ratio (GC–FID) remained constant as a function of percentage conversion of **7** because, as expected, the nitrile products are photochemically inert under the reaction conditions for their formation. Therefore the ratio obtained is a primary product ratio reflecting the facial selectivity in the nucleophilic attack of cyanide ion on the radical cation of **7**.

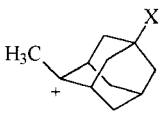
Previously reported literature values of *syn:anti* isomer ratios for a variety of reactions with very different mechanisms will put the value obtained for **7** in context. For instance (substrate, substituent, conditions, *syn:anti*): 2-adamantanone, 5-OCH_3, $NaBH_4/H_2O$/0°C, 64:36 (3); 2-adamantanone, 5-OCH_3, MeLi/ether/0°C, 63:37 (3); 2-adamantane carboxylic acid, 5-Ph, Br_2/CCl_4/40°C (Hunsdiecker reaction), 58:42 (9); 2-adamantanone, 5-F, hν, NC-CH═CH-CN, CH_3CN (Paterno–Büchi reaction), 57:43 (12). Trapping of 2-adamantyl cations gives higher *syn:anti* ratios: 2-methyleneadamantane, 5-OCH_3, HCl/CH_3NO_2/0°C, 85:14 (3); 2-methyleneadamantane, 5-F, HCl/CH_3NO_2/0°C, 100:0 (3); 2-methyladamantanol, 5-F, HCl/CH_2Cl_2/0°C, 83:13 (6).

The first observation is the relatively low variation in the *syn:anti* ratio with reaction type. For instance, in the Paterno–Büchi reaction, the product-determining step is the quenching of the excited singlet state of 2-adamantanone by the alkene; the rate constant is known to be diffusional (i.e., rate constant approaching 10^{10} M^{-1} s^{-1}). The rate is also very fast for trapping of the 2-adamantyl radical in the Hunsdiecker reaction. In contrast to these two reactions where the product ratio reflects the trapping of a reactive intermediate, the $NaBH_4$ reduction of 2-adamantanone is a relatively slow process; the product-determining step is now expressed in minutes (i.e., rate constant approximately 10^{-2} M^{-1} s^{-1}). Therefore reactions differing in rate constant by at least 10^{12} show similar facial selectivity! The reactivity/selectivity principle predicts that the photochemical reaction occurring at the diffusional limit might be expected to show considerably less selectivity and perhaps none at all.

A possible explanation for these observations is that the facial selectivity observed for the transient intermediates is a consequence of a nonplanar geometry at C2 of the adamantane ring. This is a reasonable possibility because the *n*–π* excited



22



23

singlet state of ketones (35) is, and tertiary radicals (ref. 35, pp. 264–267) may be, pyramidal. In fact, the interpretation for the very high facial selectivity observed for 2-adamantyl cations is that the substituent at C5 controls the equilibration between two diastereomeric pyramidal cations (free or intimate ion pairs), **22** and **23** (3). Because carbocations, unless they are highly stabilized, are known to be quenched by nucleophiles at the diffusional rate (36), the facial selectivity is determined

by the ratio of the concentration of **22** to that of **23** and not by their relative reactivity. The substituent exhibits a large effect because the equilibrium favors **22** over **23** as a result of the hyperconjugative interaction between the substituent and the full positive charge at the electrophilic center.

Because of these possibilities, the geometry of the radical cation of **7** is clearly an important factor to consider. MO calculations at both the AM1 level and STO–3G level[5] gave a planar geometry at C2 but this level of theory is probably not adequate to make a reliable prediction. The AM1 calculations gave spin densities of 0.50 and 0.22 at the adamantane C2 and the diphenylmethylene carbon, respectively; in contrast, the charge densities (0.08 and 0.09) are both very low. Thus, the radical cation of **7** might be expected to show the low facial selectivity characteristic of a radical reaction rather than that of a cation. This is indeed the case, the 58:42 *syn*:*anti* ratio being the same as that observed in the trapping of the 2-adamantyl radical by Br_2 (9). The regioselectivity for the addition of cyanide ion to the radical cations of both **6** and **7** highly favors nucleophilic attack at the endocyclic carbon. Because the charge density is essentially identical at these two carbons, this observation may reflect the higher stability of the product diphenylmethyl radical over the other possibility, the tertiary 2-adamantyl radical. For 1,1-diphenylethylene, the radical cation reacts exclusively at the C2 but, in this case, the calculated charge density is considerably higher at that carbon (0.21 versus 0.12 at the diphenylmethyl carbon) (37).

Experimental

General experimental

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform ($CDCl_3$) on either a Bruker AC 250F NMR spectrometer in automation mode or, as indicated, on an AMX 400 wide-bore NMR spectrometer. Proton chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (0.00) as an internal standard. Reported coupling constants are experimental values. In many cases, coupling between ring protons in the adamantyl systems was unresolved, and the chemical shifts were reported as singlets. Carbon chemical shifts are reported relative to deuterated chloroform (triplet centred at δ 77.07). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Carbon multiplicities were assigned from either DEPT with multiplicity analysis (DEM) or J modulation (JMOD) experiments.

Electron-impact mass spectra (MS) were run at 70 eV ionizing energy, either on a CEC 21-104 single focussing or a CEC 21-110B double focussing mass spectrometer. Ionizing energies are reported in parentheses for spectra not run at 70 eV. Samples were introduced directly into the mass spectrometer source using a glass or quartz probe and were heated until an adequate ion current was observed. Masses are reported as mass/charge (*m*/*z*) ratios. Ion intensities are given in parentheses relative to the base peak intensity (100). The molecular ion is indicated by M. Accurate mass determinations were made on the CEC 21-110B spectrometer with perfluorokerosene (PFK) as an internal standard at a resolution of approximately 10 000. Chemical ionization mass spectra (CIMS) were run on a Fisons/VG Quattro triple quadrupole mass spectrometer, using isobutane as the ionizing gas. Spectra are reported in the normal manner.

Ultraviolet (UV) spectra were obtained in acetonitrile–methanol on a Varian Cary 219 spectrometer using a 1 cm quartz cuvette. Wavelength maxima (λ_{max}) are reported in nanometres. Infrared (IR) spectra were obtained on a Nicolet 205 FT-IR spectrometer. Samples were run either neat or as a Nujol mull on sodium chloride plates. Frequencies are reported in wave numbers (cm^{-1}). Melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. Combustion analyses were carried out by Canadian Microanalytical Services Ltd., Delta, B.C., Canada.

GC–MS analyses were done on a Hewlett–Packard 5890A GC and a 5970 mass selective detector. The column used was 5% phenyl methyl silicon on fused silica with a film thickness of 0.25 μm and column dimensions of 25 m × 0.2 mm. Masses are reported in the same manner as described above. GC–FID analyses were carried out on a Perkin–Elmer Autosystem gas chromatograph using either a DB-5 column, 15 m × 0.53 mm, with a film thickness of 1.5 μm, or a BT-1 100% polymethylsilicone column, 12 m × 0.22 mm, with a film thickness of 0.25 μm. Data were analyzed using computer software written in-house. HPLC analyses were done using a Waters 6000 solvent delivery system and a Waters U6K injector under isocratic conditions with a flow rate of 2 mL/min using a Brownlee Lab Spheri-10 10 μL reverse-phase column (25 × 0.46 cm) with a Waters model 450 variable wavelength detector. UV detection was at either 254 or 280 nm.

Column chromatography was carried out using silica gel (60 Å, 70–230 mesh) from the Aldrich Chemical Company. Column solvents, hexane and ethyl acetate, were distilled prior to use. Fractions were monitored by either GC–FID or thin-layer chromatography (tlc) using silica-coated polyester plates, purchased from the Aldrich Chemical Company.

The following compounds were purchased from the Aldrich Chemical Company: benzilic acid, phenyl isothiocyanate, 4-*tert*-butylcyclohexanone, *p*-toluenesulfonic acid, 2-adamantanone, tris(diethylamino)phosphine, magnesium turnings, benzyl chloride, 4-methoxybenzyl chloride, 5-hydroxy-2-adamantanone, methyl iodide, sodium hydride (56–58% suspension in oil), 1.0 M borane – tetrahydrofuran complex, tetraethylammonium cyanide. These chemicals were used without further purification unless otherwise noted.

Synthesis of alkenes 2, 6, and 7

Thiobenzylic acid

The following procedure was adapted from that reported by Becker and Bistrzycki (38). Benzilic acid was recrystallized from water prior to use. Benzilic acid (8.88 g, 0.039 mol) and phenyl isothiocyanate (7.49 g, 0.055 mol) were combined, and were ground to a slurry using a mortar and pestle. After the slurry was transferred to an Erlenmeyer flask, glacial acetic acid (10 mL) was added as solvent and the mixture was stirred and cooled to 0°C in an ice–water bath. Concentrated sulfuric acid (5 mL) was added dropwise, and the resulting red slurry stirred at 0°C for 2 h, then at room temperature for 2 h longer. Stirring was stopped, and the mixture was left to sit overnight. The resulting pink paste was poured into a beaker of crushed

[5] M.S.W. Chan, Department of Chemistry, Dalhousie University, unpublished results, 1997.

ice, and the solid collected by suction filtration. Recrystallization from methanol–water gave the intermediate product, $PhN(H)C(O)SC(Ph)_2CO_2H$, as colourless crystals (8.80 g, 62% yield); mp 144–146°C (lit. (38) mp 140.5°C).

The product from above (8.80 g, 0.024 mol) was refluxed in 10% KOH (300 mL) for 5 h. After cooling, the solution was gravity filtered to remove a white solid. The filtrate was then acidified with aqueous hydrochloric acid and the resulting solid was collected by suction filtration. Recrystallization from 50% acetic acid gave thiobenzilic acid as white needles (5.17 g, 87% yield); mp 149–151°C (lit. (40) 147.5–149°C).

5-Methoxy-2-adamantanone

Sodium hydride (15 mol% excess), was washed with hexanes, then added to a stirred solution of 5 hydroxy-2-adamantanone (1.0 g, 0.060 mol) in dimethyl sulfoxide (DMSO, 15 mL). The solution became cloudy, and vigorous bubbling was observed. After 30 min methyl iodide (15 mol% excess) was added dropwise and the solution left to stir until clear (overnight). The reaction was quenched with water and extracted three times with dichloromethane. The combined organic layers were washed three times with water and twice with brine to remove the DMSO, then dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The crude ether (81%) was purified by column chromatography (10:90 ethyl acetate:hexane). ^{13}C NMR data of the isolated oil agreed with literature values (34).

1,3-Oxathiolan-5-ones

This procedure was developed by Barton and Willis (17). Thiobenzilic acid (4.1 mmol), *p*-toluenesulfonic acid (1.5 mmol), and the appropriate ketone (4.1 mmol) were combined in a round-bottom flask fitted with a Dean–Stark trap and condenser. Benzene (70 mL) was added as solvent. The mixture was refluxed (5–8 h) under nitrogen with azeotropic removal of water. The resulting solution was cooled, washed four times with saturated sodium bicarbonate, then with water until the aqueous layer was neutral to pH paper. The organic layer was then dried over anhydrous magnesium sulfate and the solvent was removed under vacuum. The 1,3-oxathiolan-5-ones were purified by column chromatography to give colourless solids.

4-tert-*Butylcyclohexanespiro-2'-(4',4'-diphenyl-1',3'-oxathiolan-5'-one),* **2a**

4-*tert*-Butylcyclohexanone was recrystallized from low-boiling petroleum ether prior to use. The two product diastereomers (overall yield 96%) were separated once for characterization purposes, but otherwise the mixture was used for the next step.

Isomer 1: mp 156–158°C; ^{1}H NMR (400 MHz) δ: 7.48–7.27 (m, 10H), 2.14 (d, 2H, J = 13.4 Hz), 1.72 (td, 2H, J = 14 Hz, 4 Hz), 1.65 (d, 2H, J = 13.4 Hz), 1.45 (q, 2H, J = 14 Hz), 1.01 (tt, 1H, J = 12.6 Hz, 4 Hz), 0.83 (s, 9H); ^{13}C NMR δ: 173.81, 141.09, 128.57, 128.35, 127.93, 87.63, 67.67, 46.53, 40.88, 32.35, 27.47, 24.39;

Isomer 2: mp 102–105°C; ^{1}H NMR (400 MHz) δ: 7.5–7.2 (m, 10H), 1.98 (d, 2H, J = 12.9 Hz), 1.88 (td, 2H, J = 12.9 Hz, 3.1 Hz), 1.77 (d, 2H, J = 13.1 Hz,), 1.25 (qd, 2H, J = 13.1 Hz, 3.1 Hz), 0.98 (tt, 1H, J = 12.2 Hz, 3.1 Hz), 0.86 (s, 9H); ^{13}C NMR δ: 173.46 (s), 140.93 (s), 128.33 (d), 128.24 (d), 127.803, 90.66 (s), 66.88 (s), 46.11 (d), 39.53 (t), 32.08 (s), 27.43 (q), 24.37 (t); MS *m/z*: 381 (M + 1, 11), 380 (M, 37), 337 (26), 336 (100), 335 (25), 237 (11), 199 (22), 198 (94), 170 (18), 167 (37), 166 (28), 165 (76), 121 (28), 57 (37), 54 (12), 40 (22).

Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-2'-(4',4'-diphenyl-1',3'-oxathiolan-5'-one), ***6a*** *(84% yield):* mp 120–120.5°C; ^{1}H NMR (400 MHz) δ: 7.57–7.54 (m, 4H), 7.32–7.23 (m, 6H), 2.23 (d, 2H, J = 12.2 Hz), 2.02 (d, 2H, J = 12.2 Hz), 1.89 (s, 2H), 1.87 (s, 1H), 1.81 (s, 1H), 1.68 (s, 6H); ^{13}C NMR δ: 173.78 (s), 141.26 (s), 128.52 (d), 128.37 (d), 127.91 (d), 94.89 (s), 67.35 (s), 40.22 (d), 37.17 (t), 35.09 (t), 33.97 (t), 26.22 (d), 26.13 (d); MS *m/z*: 376 (M, 16), 333 (20), 332 (100), 331 (20), 256 (13), 212 (33), 211 (28), 198 (54), 167 (16), 166 (30), 165 (98), 131 (23), 121 (26), 105 (21).

5-Methoxy-tricyclo[3.3.1.1^{3,7}]decane-2-spiro-2'-(4',4'-diphenyl-1',3'-oxathiolan-5'-one), **7a** *(32% yield, as a mixture of diastereoisomers)*

Isomer 1: mp 157–158°C; ^{1}H NMR δ: 7.5–7.4 (m, 4H), 7.4–7.2 (m, 6H), 3.19 (s, 3H), 2.2–2.05 (m, 5H), 2.05–1.99 (d, 2H), 1.8–1.6 (m, 4H), 1.6–1.4 (d, 2H); ^{13}C NMR δ: 173.05, 140.75, 128.20, 128.19, 127.80, 93.21, 70.06, 67.15, 48.23, 41.70, 40.23, 37.83, 32.72, 27.95; MS *m/z*: 406 (M, 22), 363 (25), 362 (100), 361 (27), 198 (74), 167 (30), 166 (26), 165 (64), 120 (18), 109 (54).

Isomer 2: mp 138–139°C; ^{1}H NMR δ: 7.6–7.4 (m, 4H), 7.4–7.2 (m, 6H), 3.16 (s, 3H), 2.3–2.1 (m, 5H), 1.9–1.8 (d, 2H), 1.8–1.6 (m, 4H), 1.6–1.5 (d, 2H); ^{13}C NMR δ: 172.98, 140.68, 128.20, 128.18, 127.80, 92.69, 69.71, 67.11, 48.07, 42.00, 40.73, 36.68, 33.78, 27.98; MS *m/z*: 406 (38), 363 (34), 362 (100), 361 (37), 199 (17), 198 (67), 167 (31), 166 (26), 165 (77), 120 (30), 109 (18); X-ray structure, Fig. 1.[4]

Pyrolysis of 1,3-oxathiolan-5-ones

Tris(diethylamino)phosphine (greater than 15% mol excess) and the appropriate 1,3-oxathiolan–5-one were heated in an oil bath (240–260°C) under nitrogen for 8 h. Purification of the crude reaction mixture by column chromatography (100% hexane) gave the desired alkene as a colourless solid.

4-tert-*Butyl-2-diphenylmethylenecyclohexane,* ***2****:* Recrystallized from ethanol (67% yield), mp 105–107°C; UV (3:1 CH_3CN:CH_3OH): λ_{max} 240 nm, ε 1.1 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (400 MHz) δ: 7.24–7.10 (m, 10H), 2.66 (d, 2H, J = 13.2 Hz), 1.91 (dd, 2H, J = 13.2 Hz, 3.77 Hz), 1.83 (d, 2H, J = 13.4 Hz), 1.24–1.21 (m, 1H), 1.16–1.10 (m, 2H), 0.85 (s, 9H); ^{13}C NMR δ: 143.18 (s), 139.15 (s), 134.23 (s), 129.94 (d), 127.90 (d), 126.08 (d), 48.36 (d), 32.54 (s), 32.31 (t), 29.38 (t), 27.71 (q); MS *m/z*: 305 (M + 1, 26), 304 (M, 100), 206 (11), 205 (12), 180 (33), 167 (25), 91 (19), 57 (15); HRMS calcd. for $C_{23}H_{28}$: 304.219; found: 304.218.

2-Diphenylmethylenetricyclo[3.3.1.1^{3,7}]decane, **6***:* Recrystallized from ethanol (73% yield), mp 109.5–111°C (lit. (19) mp 107–109°C); UV (3:1 CH_3CN:CH_3OH): λ_{max} 244 nm, ε 1.31 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR δ: 7.28–7.11 (m, 10H), 2.77 (s, 2H),

1.99 (s, 2H), 1.86 (s, 10H); ^{13}C NMR δ: 146.65 (s), 143.03 (s), 130.73 (s), 129.59 (d), 127.97 (d), 126.00 (d), 39.63 (t, C4, C8, C9, C10), 37.17 (t, C6), 34.42 (d, C1, C3), 28.22 (d, C5, C7); MS *m/z*: 301 (M + 1, 24), 300 (M, 100). Anal. calcd. for $C_{23}H_{24}$: C 91.95, H 8.05; found: C 91.98, H 8.07.

5-Methoxy-2-diphenylmethylenetricyclo[3.3.1.1^{3,7}]decane, ***7****:* 41% yield, UV: λ_{max} 240 nm, ε 1.10×10^4 M^{-1} cm^{-1}; ^{1}H NMR δ: 7.3–7.2 (m, 4H), 7.2–7.1 (m, 6H), 3.28 (s, 3H), 2.93 (s, 2H), 2.0–1.6 (m, 11H); ^{13}C NMR δ: 144.08 (s), 142.65 (s), 131.91 (s), 129.39 (d), 128.06 (d), 126.25 (d), 71.85 (s, C5), 48.19 (s), 42.12 (t, C4, C9), 40.56 (t, C6), 38.54 (t, C8, C10), 35.74 (d, C1, C3), 30.51 (d, C7); MS *m/z*: 331 (M + 1, 24), 330 (M, 100); HRMS calcd. for $C_{24}H_{26}O$: 330.198; found: 330.198.

Synthesis of alkenes 3, 4, and 5

Preparation of alcohols

2-Phenylmethyl-2-tricyclo[3.3.1.1^{3,7}]decanol, ***3a***
Magnesium turnings (0.33 g, 0.014 mol) and anhydrous ether (5 mL) were combined under nitrogen in an oven-dried three-neck flask equipped with a reflux condenser. A few drops of a solution of benzyl chloride (1.4 mL, 0.012 mol) in anhydrous ether (10 mL) were added via a dropping funnel. When no signs of reaction were observed, the flask was immersed in a warm water bath, a single crystal of iodine was added, and the magnesium turnings were broken into smaller pieces with a spatula, until the solution turned cloudy. The resulting solution was cooled to 0°C in an ice–water bath, and the remaining benzyl chloride was added over a period of half an hour, followed by 15 min of reflux. The solution was then cooled to 0°C followed by dropwise addition of 2-adamantanone (1.67 g, 0.011 mol) in anhydrous ether (20 mL). After the addition was complete, the resulting solution was refluxed for an additional 15 min, and cooled to room temperature. The ethereal solution was transferred to a separatory funnel containing cold, saturated ammonium chloride. The ether layer was removed, and the aqueous layer was extracted with ether. The combined ether layers were washed with water, dried over anhydrous magnesium sulfate, and the solvent removed by rotary evaporation. The crude oil was purified by column chromatography (10:90 ethyl acetate:hexane) to give the desired alcohol as a white solid (59% yield); ^{1}H NMR δ: 7.19 (s, 5H), 2.91 (s, 2H), 2.15 (d, 2H, J = 12.2 Hz), 2.04 (d, 2H, J = 12.8 Hz), 1.86 (s, 1H), 1.75–1.62 (m, 6H), 1.48 (s, 2H), 1.42 (s, 1H); ^{13}C NMR δ: 137.06, 130.35, 127.80, 126.01, 74.24, 43.59, 38.17, 36.50, 34.29, 32.66, 27.28, 27.14. The ^{1}H NMR spectrum of this alcohol agrees with that previously reported (18).

2-(4-Methoxyphenylmethyl)-2-tricyclo[3.3.1.1^{3,7}]decanol, ***4a***
Magnesium turnings (0.55 g, 0.023 mol) were activated by vigorous stirring under nitrogen for 3 days prior to reaction (39). Sufficient anhydrous ether (5 mL) was added to just cover the magnesium, and the mixture was cooled to 0°C. A few drops of a solution of 4-methoxybenzyl chloride (3.0 g, 0.019 mol) in anhydrous ether (20 mL) were added. Once the solution turned cloudy, signalling formation of the Grignard reagent, the remaining 4-methoxybenzyl chloride solution was added over a half-hour period. The resulting solution was stirred for an additional 15 min. A solution of 2-adamantanone (1.0 g, 0.007 mol) in anhydrous ether (20 mL) was added dropwise over a 1 h period. Stirring was continued overnight at room temperature, and the resulting solution worked up in the same manner as above for **3a**: ^{1}H NMR δ: 7.14 (d, 2H, J = 8.5 Hz), 6.84 (d, 2H, J = 8.5 Hz), 3.79 (s, 3H), 2.93 (s, 2H), 2.06–1.92 (m, 8H), 1.77 (d, 2H, J = 11.3 Hz), 1.68 (d, 2H, J = 11.3 Hz), 1.52 (d, 2H, J = 12.2 Hz); ^{13}C NMR δ: 158.33, 131.53, 129.16, 113.7, 74.54, 55.23,42.90, 39.27, 38.45, 36.83, 34.62, 33.02, 27.55.

5-Methoxy-2-phenylmethyl-2-tricyclo[3.3.1.1^{3,7}]decanol ***5a***
The method was the same as that used for **3a**, except that THF was used in place of ether as the solvent and, instead of heating at reflux, the solution was stirred overnight at room temperature prior to work-up. Two isomers, the (*E*) and the (*Z*) alcohol, were obtained. Spectral data were assigned based on literature data for (*E*)- and (*Z*)-5-methoxy-2-adamantanol.

(E)-Alcohol: 1H NMR δ: 7.32–7.21 (m, 5H), 3.28 (s, 3H), 3.01 (s, 2H), 2.12–2.08 (m, 5H), 1.85–1.74 (m, 6H), 1.39–1.34 (m, 3H); ^{13}C NMR δ: 136.79, 130.57, 128.46, 126.74, 74.00, 71.92, 48.40, 43.84, 41.10, 38.56, 37.85, 31.91, 29.30.

(Z)-Alcohol: ^{1}H NMR δ: 7.34–7.20 (m, 5H), 3.21 (s, 3H), 2.97 (s, 2H), 2.26–2.21 (m, 3H), 2.04–1.99 (m, 3H), 1.89 (s, 2H), 1.72–1.62 (m, 4H), 1.47–1.42 (m, 2H); ^{13}C NMR δ: 137.03, 130.54, 128.42, 126.70, 73.49, 71.51, 48.10, 43.13, 41.66, 38.94, 35.98, 33.44, 29.34.

Dehydration of alcohols
The alcohols **3a**, **4a,** and **5a** were dehydrated in benzene, in the presence of *p*-toluenesulfonic acid (10 mol%) as catalyst, using the same apparatus and procedure as for the preparation of 1,3-oxathiolan-5-ones.

2-Phenylmethylenetricyclo[3.3.1.1^{3,7}]decane, ***3****:* UV (9:1 CH_3CN:CH_3OH): λ_{max} 246 nm, ε 1.5×10^4 M^{-1} cm^{-1}; ^{1}H NMR δ: 7.26–7.16 (m, 5H), 6.18 (s, 1H), 3.16 (s, 1H), 2.49 (s, 1H), 1.99 (s, 2H), 1.93 (s, 4H), 1.86 (s, 6H); ^{13}C NMR δ: 151.26 (s, C2), 138.34 (s), 128.77 (d), 128.08 (d), 125.68 (d), 117.10 (d), 41.06 (d, C3), 39.91 (t, C4,C10), 37.28 (t, C8, C9), 32.32 (d, C1), 28.49 (d, C5, C7); MS *m/z:* 225 (M + 1, 14), 224 (M, 100), 167 (10), 129 (12), 128 (12), 91 (22). Exact Mass calcd. for $C_{17}H_{20}$: 224.156; found: 224.158. The ^{1}H NMR spectrum agrees with that reported previously (18).

2-(4-Methoxyphenylmethylene)tricyclo[3.3.1.1^{3,7}]decane, ***4****:* IR (Nujol):1609, 15.09, 1449, 1299, 1247, 1176, 1040, 867, 822, 714; UV (3:1 CH_3CN:CH_3OH): λ_{max} 250 nm, ε 2.0×10^4 M^{-1} cm^{-1}; ^{1}H NMR δ: 7.13 (d, 2H, J = 8.7 Hz), 6.84 (d, 2H, J = 8.7 Hz), 6.12 (s, 1H), 3.80 (s, 3H), 3.13 (s, 1H), 2.47 (s, 1H), 1.98 (s, 2H), 1.92 (s, 4H), 1.85 (s, 6H); ^{13}C NMR δ: 157.66 (C2), 150.27, 131.01, 129.81, 116.43, 113.51, 55.28, 40.97 (C3), 39.98 (C4, C10), 39.07 (C8, C9), 37.30 (C6), 32.26 (C1), 28.52 (C5, C7); MS *m/z*: 255 (M + 1, 22), 254 (M, 100), 121 (19). Anal. calcd. for $C_{18}H_{22}O$: C 84.99, H 8.72; found: C 84.68, H 8.63.

5-Methoxy-2-phenylmethylenetricyclo[3.3.1.1^{3,7}]decane ***5****:* UV (9:1 CH_3CN:CH_3OH): λ_{max} 243 nm, ε 1.47×10^4 M^{-1} cm^{-1};

^{1}H NMR δ: 7.29–7.16 (m, 5H), 6.20 (s, 1H), 3.32 (s, 3H), 2.69 (s, 1H), 2.27 (s, 1H), 1.89–1.72 (m, 10H); ^{13}C NMR δ: 148.59 (s), 137.94 (s), 128.61 (d), 128.05 (d), 125.90 (d), 118.37 (C11, d), 71.80 (C5, s), 48.07 (q), 42.23 (C6, t), 41.99 (C3, d), 41.45 (C9, t), 40.65 (C4, t), 38.80 (C8, t), 37.92 (C10, t), 33.23 (C7, d), 30.53 (C1, d); MS *m/z*: 255 (M + 1, 19), 254 (M, 100), 167 (13), 162 (12), 134 (12), 119 (26), 109 (20), 105 (11), 91 (14), 86 (34), 84 (50), 71 (11), 56 (19), 46 (10), 40 (10). Anal. calcd. for $C_{18}H_{22}O$: C 84.99, H 8.72; found: C 84.79, H 8.54.

Photochemistry

Either a 200 or 450 W Hanovia medium-pressure mercury lamp was used as the light source for photoreactions. Mixtures of acetonitrile and methanol were used as solvent in every case. Acetonitrile was purified by a four-step procedure: distillation from sodium hydride, distillation from phosphorus pentoxide, passage through basic alumina, and distillation from calcium hydride after 24 h reflux under nitrogen. Methanol was distilled from sodium prior to use. Dicyanobenzene (DCB) and 1,4-dicyanonaphthalene were available in our laboratory. DCB and the desired alkene were dissolved in acetonitrile–methanol in an immersion well (300 or 420 mL) equipped with a Pyrex filter. The solution was purged with nitrogen for 15 min prior to the irradiation. A positive pressure of nitrogen and magnetic stirring were maintained for the duration of the reaction. After the photolysis the solvent was removed under vacuum and the photoproducts were separated by column chromatography on silica gel and identified by spectroscopic methods.

Photoproducts

4-tert-*Butyl-1-diphenylmethylcyclohexene,* ***8****:* ^{1}H NMR δ: 7.29–7.13 (m, 10H), 5.21 (s, 1H), 4.64 (s, 1H), 2.01–1.98 (m, 2H), 1.87–1.76 (m, 2H), 1.31–.122 (m, 2H), 1.04–0.99 (m, 1H), 0.85 (s, 9H); ^{13}C NMR δ: 143.05 (s), 143.02 (s), 139.70 (s), 129.35 (d), 129.29 (d), 128.17 (d), 128.14 (d), 126.14 (d), 126.08 (d), 125.74 (d), 58.48 (s), 44.18 (s), 32.26, 30.38, 27.27 (q), 27.11, 24.51; GC–MS *m/z*: 305 (15, M + 1), 304 (M, 61), 206 (13), 205 (14), 180 (31), 168 (15), 167 (100), 166 (13), 165 (31), 141 (10), 129 (19), 128 (13), 117 (11), 115 (15), 91 (51), 57 (47).

2-Phenylmethyl-2-tricyclo[3.3.1.1^{3,7}]decanenitrile, ***9****:* Recrystallized from ethanol–water, mp 105–106.5°C; ^{1}H NMR δ: 7.32–7.24 (m, 5H), 3.08 (s, 3H), 2.24 (d, 2H, *J* = 13.4 Hz), 2.16 (d, 2H, *J* = 14.0 Hz), 1.92 (s, 4H), 1.83 (s, 1H), 1.76 (s, 4H), 1.70 (s, 1H); ^{13}C NMR δ: 135.80, 130.20, 128.26, 127.14, 123.81, 46.31, 40.09, 38.05, 35.35, 33.15, 31.05, 26.96, 26.81; MS *m/z*: 252 (M + 1, 11), 251 (M, 67), 91 (100). Anal. calcd. for $C_{18}H_{21}N$: C 86.01, H 8.42; found: C 86.14, H 8.42. X-ray structure, Fig. 2.[4]

2-Phenyl-2-(2-tricyclo[3.3.1.1^{3,7}]decanyl)ethanenitrile, ***10****:* Recrystallized from ethanol–water, mp 140.5–142°C; ^{1}H NMR δ: 7.44–7.21 (m, 5H), 3.73 (s, 2H), 2.58 (s, 2H), 2.10 (s, 1H), 2.05 (s, 2H), 1.98 (s, 1H), 1.90 (s, 2H), 1.86 (s, 2H), 1.72 (s, 4H), 1.64 (s, 2H); ^{13}C NMR δ: 144.23 (s), 128.72 (d), 126.59 (d), 126.11 (d), 117.88 (s), 44.91 (s), 38.32 (t), 32.84 (t), 30.50 (t), 27.55 (d), 26.95 (d); MS *m/z*: 251 (M, 6), 212 (17), 211 (100, M – CH_2CN), 91 (11); HRMS calcd. for $C_{18}H_{21}N$: 251.167; found: 251.66. X-ray structure, Fig. 3.[4]

Methyl 1-phenyl-2-(2-tricyclo[3.3.1.1^{3,7}]decanyl)ethyl ether, ***11***

This ether was not isolated from the photoreaction of **3** but was prepared as follows.

1-Phenyl-2-(2-tricyclo[3.3.1.1^{3,7}]decanyl)ethanol

A solution of alkene **22** (0.10 g, 4.46×10^{-4} mol) in THF (15 mL) was cooled to 0°C in an ice–water bath with stirring. Borane (1.0 M solution in THF, 2.5 mL, 0.0025 mol) was added dropwise and the resulting solution was warmed to room temperature and stirred for several hours. The reaction was then opened to the air, and water (1 mL), followed by aqueous sodium hydroxide (3 M, 2 mL), was added dropwise. Vigorous bubbling was observed. Hydrogen peroxide (30% solution, 2 mL) was added dropwise, after which the solution was left to stir for 5 min at 0°C, then for 20 min at room temperature. Water (10 mL) and ether (20 mL) were added to the reaction flask and the resulting mixture was left to stir for several minutes. The solution was transferred to a separatory funnel leaving a white solid behind, and was extracted three times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the solvent removed under vacuum. Purification by column chromatography (95:5 hexane:ethyl acetate) gave the desired alcohol (0.10 g, 91% yield); ^{1}H NMR δ: 7.41–7.22 (m, 5H), 4.84 (d, 1H, *J* = 10.4 Hz), 2.32 (s, 1H), 2.08 (d, 1H, *J* = 12.8 Hz), 1.93–1.49 (m, 11H), 1.44 (d, 1H, *J* = 10.7 Hz), 1.20 (s, 1H); ^{13}C NMR δ: 144.05, 128.45, 127.67, 126.73, 74.69, 51.43, 39.06, 38.81, 38.25, 32.24, 31.66, 28.89, 28.19, 28.01, 27.84.

The ether **11** was prepared from the above alcohol by the same procedure as 5-methoxy-2-adamantone, above: ^{1}H NMR δ: 7.34–7.25 (m, 5H), 4.31 (d, 1H, *J* = 10.4 Hz), 3.16 (s, 3H), 2.35 (s, 1H), 2.05 (d, 1H, *J* = 12.8 Hz), 1.94–1.53 (m, 11H), 1.44 (d, 1H, *J* = 10.4 Hz); ^{13}C NMR δ: 141.49, 128.27, 127.55, 127.47, 84.26, 56.76, 50.88, 39.14, 38.82, 38.34, 31.96, 30.09, 29.42, 28.32, 28.16, 27.95; GC–MS *m/z*: 122 (16), 121 (100), 91 (23), 79 (12), 77 (24).

Methyl 2-phenylmethyl-2-tricyclo[3.3.1.1^{3,7}]decanyl ether, ***12****:* Recrystallized from ethanol, mp 101–103°C; ^{1}H NMR δ: 7.31–7.19 (m, 5H), 3.34 (s, 3H), 3.00 (s, 2H), 2.12–2.00 (m, 4H), 1.91–1.69 (m, 8H), 1.46 (d, 2H); ^{13}C NMR δ: 137.92, 130.19, 128.02, 125.97, 79.57, 47.34 (C2), 38.42 (C6), 35.21 (C4,C9), 34.53 (C1,C3), 33.63 (C8,C10), 32.80 (C11), 27.70 (C7), 27.29 (C5); MS (70 eV) *m/z*: 165 (100, M – C_7H_7), 91 (19); MS (20 eV) *m*/z: 256 (M, 1), 166 (12), 165 (100), 91 (19), 81 (10), 79 (11); CIMS (iso-C_4H_{10}) *m/z*: 257 (4), 226 (18), 225 (100), 185 (10), 165 (37).

2-(4-Methoxyphenylmethyl)-2-tricyclo[3.3.1.1^{3,7}]decanenitrile, ***13****:* mp 96–98°C; ^{1}H NMR δ: 7.27 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 8.5 Hz), 3.79 (s, 3H), 3.03 (s, 2H), 2.24 (d, 2H, *J* = 12.8 Hz), 2.15 (s, 2H, *J* = 13.4 Hz), 1.92 (s, 4H), 1.83 (s, 1H), 1.76 (s, 4H), 1.69 (s, 1H); ^{13}C NMR δ: 158.72, 131.18, 127.80, 123.98, 113.66, 55.19, 46.51, 39.24, 38.07, 35.39, 33.09, 31.04, 27.00, 26.85; MS *m/z*: 281 (M, 100), 121 (100); HRMS calcd. for $C_{19}H_{23}NO$: 281.178; found: 281.180.

2-(4-Methoxyphenyl)-2-(2-tricyclo[3.3.1.1^{3,7}]decanyl)ethanenitrile, ***14****:* ^{1}H NMR δ: 7.32 (d, 2H, *J* = 8.7 Hz), 6.92 (d, 2H, *J* = 8.7 Hz), 3.81 (s, 3H), 2.73 (s, 2H), 2.74 (s, 2H), 2.06 (d, 2H, *J* = 14.6 Hz), 1.98 (s, 1H), 1.88 (d, 2H, *J* = 11.6 Hz), 1.73 (s, 2H), 1.63 (s, 1H), 1.57 (s, 4H); MS *m/z*: 281 (M, 10), 242 (22), 241 (100, M – CH_2CN), 130 (34), 128 (23), 121 (20), 102 (15), 85 (19), 56 (39), 55 (11), 54 (26), 42 (42), 40 (43), 38 (15), 29 (28), 38 (24); HRMS calcd. for $C_{19}H_{23}NO$: 281.178;found: 281.176.

Methyl 2-(4-methoxyphenylmethyl)-2-tricyclo[3.3.1.1^{3,7}]-decanyl ether, ***15****:* mp 81–82.5°C; IR (Nujol): 2227, 1611, 1511, 1444, 1251, 1177, 1030; ^{1}H NMR δ: 7.15 (d, 2H, *J* = 8.5 Hz), 6.82 (d, 2H, *J* = 8.5 Hz), 3.78 (s, 3H), 3.33 (s, 3H), 2.94 (s, 2H), 2.10 (d, 2H, *J* = 12.2 Hz), 2.00 (d, 2H, *J* = 12.2 Hz), 1.90 (s, 1H), 1.76 (s, 4H), 1.68 (s, 2H), 1.57 (s, 1H), 1.45 (d, 2H, *J* = 11.9 Hz); ^{13}C NMR δ: 157.85, 131.00, 129.88, 113.49, 79.52, 55.24, 47.30, 38.42, 34.51, 34.30, 22.56, 32.81, 27.72, 27.32; MS *m/z*: 254 (M, 28),166 (10), 165 (100), 121 (10); HRMS calcd. for $C_{19}H_{26}O_2$: 286.193; found: 286.192.

Methyl 1-(4-methoxyphenyl)-2-(2-tricyclo[3.3.1.1^{3,7}]decanyl)-ethyl ether, ***16****:* ^{1}H NMR δ: 7.21 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 4.26 (d, 1H, *J* = 10.4 Hz), 3.81 (s, 3H), 3.13 (s, 3H), 2.31–1.56 (m, 14H); ^{13}C NMR δ: 159.05, 133.42, 128.56, 113.65, 83.74, 56.59, 55.25, 50.83, 39.18, 38.84, 38.37, 32.27, 31.97, 28.80, 28.37, 28.18, 27.97; MS *m/z*: 286 (M, 5), 152 (10), 151 (100).

2-(Diphenylmethyl)-2-tricyclo[3,3,1,1^{3,7}]decanitrile, ***17****:* mp 256–257.5°C; ^{1}H NMR δ: 7.7–7.6 (m, 4H), 7.4–7.2 (m, 6H), 4.61 (s, 1H), 2.35–2.15 (m, 4H), 1.94 (bs, 4H), 1.9–1.7 (m, 4H), 1.7–1.6 (d, 2H); ^{13}C NMR (250 MHz) δ: 139.40 (s), 129.37 (d), 128.59 (d), 127.19 (d), 123.95 (s, CN), 52.40 (d, Ph_2CH), 48.01 (s, C2), 38.22 (t, C6), 35.15 (t, C8,C10), 32.02 (d, C1, C3), 30.86 (t, C4,C9), 26.61 (d, C5 or C7), 26.58 (d, C5 or C7). Assignments in the ^{13}C spectrum were based on an NOE experiment; irradiation of the diphenylmethyl C-H gave enhancements only for the *ortho* aromatic hydrogens and a doublet at δ 2.19. An ^{1}H/^{13}C correlated spectrum demonstrated that the proton was attched to C4 at δ 30.86. MS *m/z:* 327 (M, 7), 210 (12), 168 (16), 167 (100), 108 (14), 105 (27), 91 (16), 77 (10); HRMS calcd. for $C_{24}H_{25}N$: 327.199; found: 327.198. The X-ray structure is shown in Fig. 4.[4]

1,2-Diphenyl-2-(2-tricyclo[3.3.1.1^{3,7}]ethanenitrile, ***18****:* GC–MS *m/z*: 212 (13), 211 (100), 167 (20), 129 (10), 91 (38).

syn-*5-Methoxy-2-(diphenylmethyl)-2-tricyclo[3.3.1.1^{3,7}]-decanenitrile,* ***19****:* mp 176–178°C; ^{1}H NMR δ: 7.7–7.6 (m, 4H), 7.5–7.2 (m, 6H), 4.51 (s,1H), 3.23 (s, 3H), 2.4–2.1 (m, 6H), 1.8–1.6 (m, 7H); ^{13}C NMR (250 MHz) δ: 138.95 (s), 129.30 (d), 128.70 (d), 127.38 (d), 123.50 (CN), 70.66 (s, C5), 52.43 (d, Ph_2CH), 48.17 (q), 47.45 (s, C2), 40.73 (t, C6), 35.06 (t, C4,C9), 34.87 (d, C1,C3), 34.08 (t, C8,C10), 28.78 (d, C7); MS *m/z:* 357 (M, 2), 168 (28), 167 (100), 165 (22); HRMS calcd. for $C_{25}H_{27}NO$: 357.209; found: 357.210. The X-ray structure is shown in Fig. 5.[4]

anti-*5-Methoxy-2-(diphenylmethyl)-2-tricyclo[3.3.1.1^{3,7}]-decanenitrile,* ***20****:* mp 148–149°C; ^{1}H NMR δ: 7.7–7.6 (d, 4H), 7.4–7.2 (m, 6H), 4.52 (s, 1H), 3.28 (s, 3H), 2.3–2.1 (m, 6H), 1.8–1.6 (m, 7H); ^{13}C NMR (250 MHz) δ: 138.95 (s), 129.30 (d), 128.70 (d), 127.39 (d), 123.34 (CN), 70.66 (s, C5), 52.43 (d, Ph_2CH), 48.17 (q, CH_3O), 47.45 (s, C2), 40.72 (d, C6), 35.06 (t, C4, C9), 34.88 (d, C1, C3), 34.08 (t, C8, C10), 28.78 (d, C7); MS *m/z:* 357 (M, 2), 168 (19), 167 (100), 165 (19); HRMS calcd. for $C_{25}H_{27}NO$: 357.209; found: 357.209.

1,2-Diphenyl-2-(5-methoxy-2-tricyclo[3.3.1.1^{3,7}]ethanenitrile, ***21****: GC–MS m/z:* 242 (19), 241 (100, 2-phenyl-5-methoxy-2-adamantyl$^+$), 167 (10), 109 (22), 91 (19).

Photolysis of 3 in methanol-OD

The photoreaction of alkene **3** in the presence of added cyanide ion was repeated on 0.10 g of the alkene using deuterated methanol, CH_3OD. The reaction was stopped at low percentage conversion, and the photoproducts were not separated. The percentage deuterium in the products was obtained using the Single Ion Monitoring (SIMS) program on the GC–MS and software developed in-house.

Fluorescence quenching studies

A Perkin–Elmer MFP 66 fluorescence spectrometer at 25°C was used for fluorescence measurements. Samples were prepared with constant concentration of the sensitizer, either DCB or 1,4-dicyanonaphthalene, and varying concentration of alkene in either 9:1 or 3:1 acetonitrile:methanol. All samples were degassed by three freeze–pump–thaw cycles.

Cyclic voltametric measurements

Cylic voltammetry at a sweep rate of 100 mV/s was used to obtain the oxidation potentials of the alkenes. The apparatus has been described previously (40). The working electrode was a platinum sphere (1 mm diameter) and the counter electrode was a platinum wire. The reference electrode was saturated calomel (SCE), which was connected to the solution (0.1 M TEAP, acetonitrile) through a Luggin capillary. The alkene concentration was ca. 0.005 M. Because the anodic wave was irreversible, the half-wave potential was taken as 0.028 V before the peak potential (41).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for the financial support that made this work possible. S.S. thanks the Dalhousie Faculty of Graduate Studies for the award of a graduate fellowship. We also thank Dr. Peter de Lijser for the measurement of oxidation potentials and Professor D.R. Arnold for helpful discussions.

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