The tandem intermolecular Paternò–Büchi reaction: formation of tetrahydrooxepins

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The Paternò–Büchi reaction is the [2 + 2] photocycloaddition between carbonyl compounds and electron rich alkenes to generate oxetane products. By the introduction of substituted cyclopropyl rings to the alkene components, the utility of this reaction has been extended to facilitate the synthesis of substituted tetrahydrooxepins. It is proposed that initial addition of oxygen radicals to cyclopropyl enol ethers generates cyclopropylmethyl radicals which, when the cyclopropane ring bears appropriate radical-stabilising groups (*e.g.* phenyl, CO_2Et), undergo rapid fragmentation to form homoallylic 1,7-biradicals which then recombine to deliver the observed tetrahydrooxepin products. The importance of various radical-stabilising substituents on the efficiency of tetrahydrooxepin formation is examined.

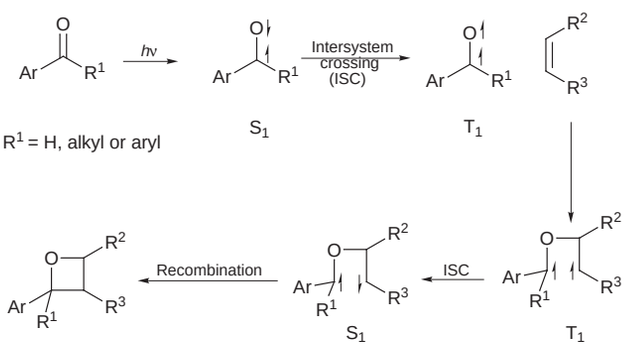
Introduction

In 1909, Paternò and Chieffi discovered that when a mixture of benzaldehyde and 2-methylbut-2-ene was irradiated, a novel small ring heterocycle, namely an oxetane ring, was formed.[1] The structure of this product was not confirmed until 1954 when Büchi and co-workers reinvestigated the reaction.[2] Initially, the Paternò–Büchi reaction was not widely accepted by synthetic organic chemists and it was not until the reviews of both Hammond and Turro in 1963[3] and Searles in 1964[4] that the usefulness of the Paternò–Büchi reaction in organic synthesis was clearly demonstrated. This photochemical method can now be used to overcome a number of the complexities associated with other methods for oxetane formation and the use of the Paternò–Büchi reaction for the formation of oxetane rings is now well established.[5,6]

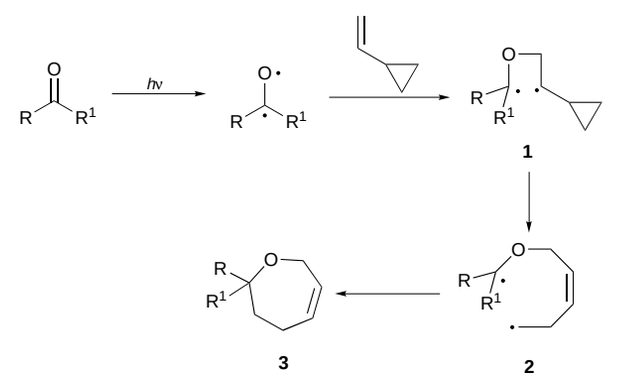
The Paternò–Büchi reaction can be employed in both intra- and inter-molecular reactions and has been reported to give products with high chemo-, regio- and diastereo-selectivity.[7–10] The starting materials are generally readily available and the yields ranges from medium to quantitative. It can also be applied to other unsaturated systems other than alkenes, such as dienes,[11] allenes,[12] acetylenes[13] and ketenimines.[12] Due to their strain and basicity, oxetane rings have been shown to be useful synthetic intermediates and some transformations of the oxetane ring include hydrogenolysis,[9] ring opening through inter-[10] and intra-molecular[14] nucleophilic attack and ring expansion.[15]

The mechanism proposed for the formation of oxetanes using the Paternò–Büchi reaction is outlined in Scheme 1.[5,11,16] Upon irradiation with ultra-violet light (280–400 nm), the carbonyl group is excited in an n–π* transition from the ground state (S_0) to the singlet excited state (S_1). For an aromatic carbonyl compound, the S_1 biradical very efficiently undergoes an intersystem crossing (ISC) to the triplet excited state (T_1). The excited oxygen radical then adds to the olefinic component, generating a 1,4-biradical which, after intersystem crossing back to a singlet state, recombines to generate the observed oxetane products.

Given that the accepted mechanism for the Paternò–Büchi reaction involves the intermediacy of both 1,2- and 1,4-biradicals, we proposed that by incorporation of cyclopropyl rings at appropriate locations on either the carbonyl or olefinic component of the Paternò–Büchi reaction, methylene cyclopropyl radicals could be generated as intermediates in these reactions. Cyclopropyl ring fragmentation of these intermediates might then be followed by radical recombination to deliver oxepane-type products (Scheme 2). For a 1,4-biradical (*viz*. **1**)



Scheme 1



Scheme 2

to undergo ring opening, the alkene substrate must bear an α-cyclopropyl ring moiety. Ring fragmentation of cyclopropyl methyl radical **1** would then lead to a homoallylic 1,7-biradical intermediate **2** which could cyclize to generate the oxepane product **3**. For the 1,7-biradicals (**2**) to cyclize, geometrical isomerism of the alkene formed after cyclopropyl ring fragmentation must be taken into consideration and we expected that while both geometrical isomers of **2** might be formed,

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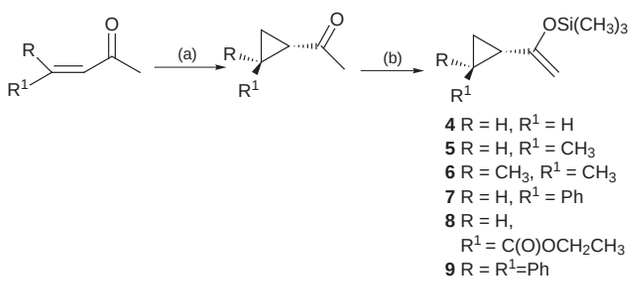
only the (*Z*)-isomers would be productive in terms of oxepane formation.[17,18]

Oxepane formation *via* cyclopropyl ring fragmentation has been observed previously by Nishida,[17] Wagner[18] and Neckers,[19] respectively, in a process that makes use of an intermolecular Paternò–Büchi reaction.[17–19] Ring fragmentation was achieved at high temperatures and the effect of substituents on the alkene and carbonyl components were investigated. Since this report, studies of the rates of cyclopropyl radical fragmentation have shown that ring opening of cyclopropyl methyl radicals is heavily influenced by the nature of the substituents on the cyclopropyl ring.[20] In terms of our own goals, the available data on cyclopropyl ring fragmentation rates supported the notion that fragmentation–oxepane formation pathways might be able to compete effectively with Paternò–Büchi-like oxetane formation. In this article we report on the results of our studies where we demonstrate that appropriately substituted Paternò–Büchi reaction partners are able to serve as precursors to substituted oxepane products.

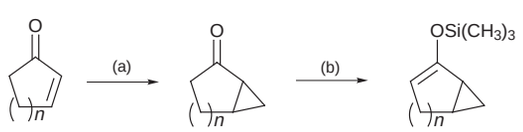
Results and discussion

Synthesis of cyclopropyl silyl enol ethers

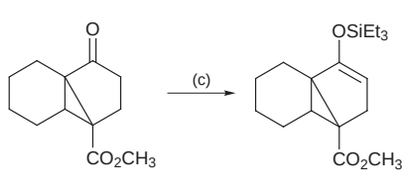
Initially we chose to investigate the generation of tetrahydrooxepin systems employing α-cyclopropyl silyl enol ethers in tandem reactions with various aromatic ketones and aldehydes (*cf*. Scheme 2). The various cyclopropyl silyl enol ethers that were used in these studies are shown in Scheme 3. In order to



4 R = H, R^1 = H
5 R = H, R^1 = CH_3
6 R = CH_3, R^1 = CH_3
7 R = H, R^1 = Ph
8 R = H,
R^1 = $C(O)OCH_2CH_3$
9 R = R^1=Ph



10 *n* = 1
11 *n* = 2



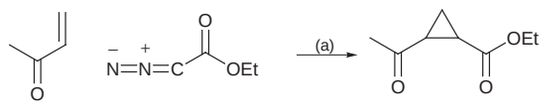
13 **12**

Scheme 3 *Reagents and conditions*: (a) $(CH_3)_3S(O)I$/NaH, DMSO, RT; (b) LDA then $(CH_3)_3SiCl$, THF, −78 °C; (c) KH, Et_3Cl, 1,4-dioxane, reflux

promote fragmentation and oxepane formation, all these compounds carried the common feature of a cyclopropyl ring adjacent to the silyl enol ether moiety. These ethers included monocyclic **4**–**9**, bicyclic **10**,**11** and tricyclic system **12** and the varying substituents attached to the cyclopropyl ring were installed to allow us to investigate the relative fragmentation efficiency of primary, secondary, tertiary and benzylic radical intermediates.

The mono- (**4**–**7**) and bi-cyclic ethers (**10**,**11**) were prepared as shown in Scheme 3 from commercially available α,β-unsaturated ketones [except for **4** (R, R^1 = H), where cyclopropyl methyl ketone was commercially available]. In most cases, the α,β-unsaturated ketones were reacted with a mixture of trimethylsulfoxonium iodide and sodium hydride to give appropriate cyclopropyl ketones.[21] The tricyclic silyl enol ether **12** was prepared by heating ketone **13**[22] at reflux in 1,4-dioxane in the presence of potassium hydride and triethylsilyl chloride.

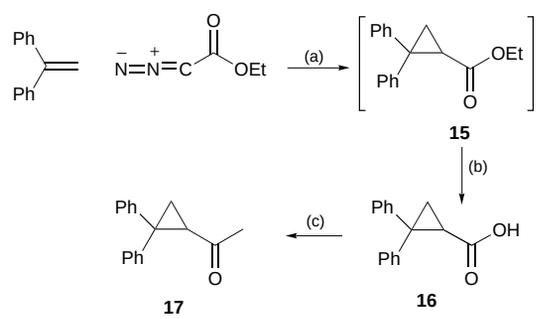
Ester **8** and diphenylcyclopropyl silyl enol ether **9** were prepared using ethyl diazoacetate as a cyclopropanation agent. Thus, reaction of ethyl diazoacetate with methyl vinyl ketone in the presence of a catalytic amount of palladium(II) acetate gave the known[23] cyclopropyl methyl ketone **14** in 51% yield (Scheme 4). Conversion to the silyl enol ether was accomplished using standard conditions to give enol ether **8** in 31% yield.



14

Scheme 4 *Reagents and conditions*: (a) $Pd(OAc)_2$, 40 °C to room temperature

In the synthesis of diphenyl silyl enol ether **9**, ethyl diazoacetate was heated in 1,1-diphenylethene to give the ester **15** which was not isolated but hydrolysed with potassium hydroxide to provide the carboxylic acid **16** (60%) (Scheme 5).[24] This



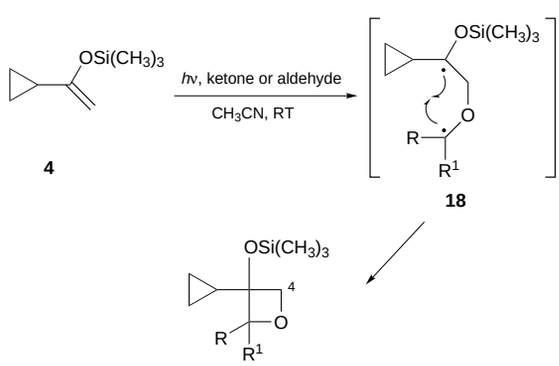
15 **16** **17**

Scheme 5 *Reagents and conditions*: (a) 160 °C; (b) KOH (aq.) then H_3O^+; (c) CH_3Li

carboxylic acid was then treated with methyllithium to give the required diphenylcyclopropyl methyl ketone **17** (88%).[25] Ketone **17** was then subjected to enolisation/trapping (LDA–TMSCl) conditions as above to generate the cyclopropyl enol ether **9** (93%).

Photoreactions of monocyclic cyclopropyl silyl enol ethers

The unsubstituted cyclopropyl silyl enol ether **4**, when irradiated in the presence of either benzophenone or 4-cyanobenzaldehyde delivered the 3-substituted oxetane products **19** (73%) and **20** (46%) respectively (Scheme 6). The regiochemical



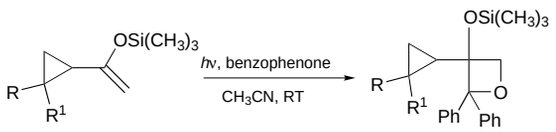
18

19 R = R^1 = Ph
20 R = H, R^1 = *p*-C_6H_4CN

Scheme 6

outcome of these reactions was predicted based on previously reported experiments and revealed that initial addition of the oxygen radical to the least substituted olefinic carbon generated the 1,4-biradical **18** which then underwent recombination to give the observed oxetane products **19** and **20**.[26]

In a similar manner, reaction of mono- and di-methylcyclopropyl silyl enol ethers **5** and **6** with benzophenone delivered the 3-substituted oxetane compounds **21** and **22** respectively as inseparable mixtures of diastereoisomers (Scheme 7). Thus, reactions of mono-, di- and un-substituted



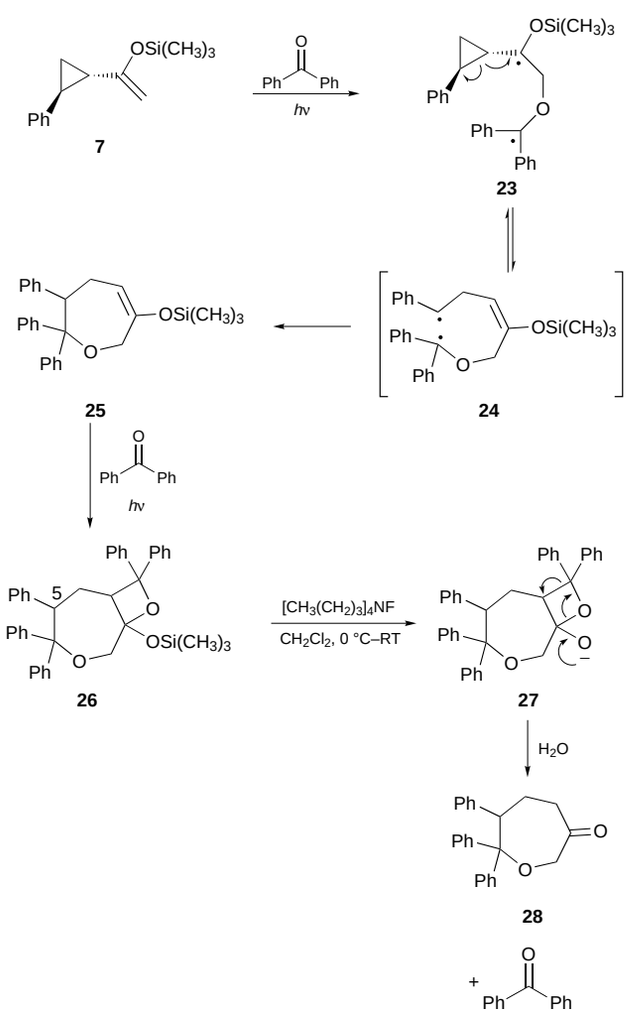
5 R = H, R^1= CH_3
6 R = R^1 = CH_3

21 R = H, R^1 = CH_3
22 R = R^1 = CH_3

Scheme 7

cyclopropyl silyl enol ethers **4**–**6** failed to deliver any ring-opened oxepane products.

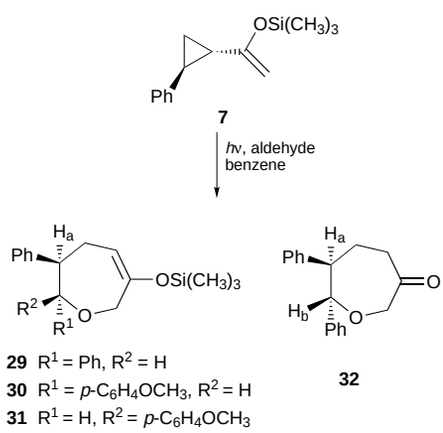
While all previous photochemical reactions had exclusively delivered oxetane-bearing products, it was highly satisfying to observe that Paternò–Büchi reaction of the mono-phenyl substituted cyclopropyl enol ether **7** with benzophenone gave a product whose structure was consistent with that of ring-opened compound **26** (15%) (Scheme 8). The structure of **26** was identified by a number of spectroscopic techniques. The 100 MHz $\{^1H\}^{13}C$ NMR spectrum of compound **26** displayed a



Scheme 8

distinct peak at δ 103, indicating the presence of an acetal carbon, and supported the contention that the second oxygen radical addition had occurred at the most substituted olefinic position of **25**. Two methylene carbon resonances appeared at δ 31.9 and δ 71.1 as well as five aromatic quaternary carbon signals. Heteronuclear ($^1H/^{13}C$) correlation spectroscopy (HETCOSY) established that the two methine carbons of **26** had the same chemical shift at δ 50.3.

Oxepane **26** was apparently formed by addition of the benzophenone oxygen-centred radical to the less substituted carbon of alkene **7**, giving rise to a cyclopropylmethyl radical **23**. Rapid fragmentation of the cyclopropyl ring to give a 1,7-biradical intermediate **24** followed by radical recombination delivered the putative intermediate tetrahydrooxepin derivative **25**. A second molecule of benzophenone then underwent photoaddition to the more substituted carbon of enol ether **25** to deliver the observed dioxabicyclo[5.2.0]nonane **26**. Despite extensive spectroscopic examination of **26**, we are currently unable to assign the relative stereochemistry of the oxetane ring and the C5-phenyl group in this compound. Treatment of compound **26** with tetrabutylammonium fluoride removed the silyl group to give a tertiary alkoxide **27** which spontaneously underwent oxetane ring-opening to give the ketone **28** (82%) and benzophenone. The outcome of this reaction further confirmed the structure of the photoaddition product **26**. This result indicated that when a sufficiently stable biradical intermediate could be generated by cyclopropyl fragmentation (*e.g.* **24**), oxepane products may be generated from carbonyl compounds and silyl enol ethers in a single step. In order to investigate the scope of this new tandem radical reaction, silyl enol ether **7** was further reacted with both benzaldehyde and 4-methoxybenzaldehyde. Reaction with benzaldehyde gave the tetrahydrooxepin product **29** (27%) and oxepanone **32** (6%) (Scheme 9). The two phenyl groups of **29** and **32** were expected



29 R^1 = Ph, R^2 = H
30 R^1 = *p*-$C_6H_4OCH_3$, R^2 = H
31 R^1 = H, R^2 = *p*-$C_6H_4OCH_3$

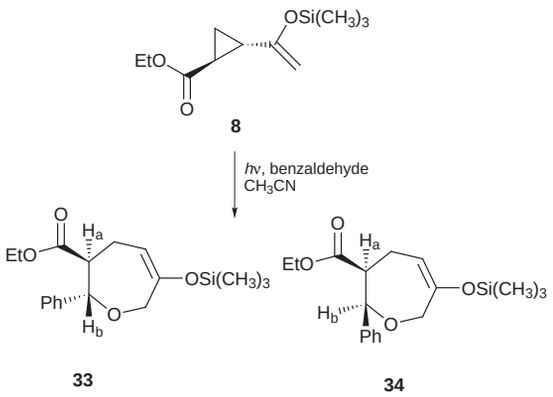
32

Scheme 9

to reside on opposite faces of the oxepane ring and this prediction was supported by the observation of a 10.2 Hz coupling constant in the 400 MHz ^1H NMR spectrum between H_a and H_b for both **29** and **32**. The most likely source of ketone **32** is by proto-desilylation of **29** during work-up and isolation. Photoreaction of 4-methoxybenzaldehyde with silyl enol ether **7** gave the diastereoisomeric tetrahydrooxepin products **30** (40%) and **31** (12%) (Scheme 9). The stereochemistry of both **30** and **31** was again assigned by looking at the coupling constants between H_a and H_b in the 400 MHz ^1H NMR spectra. The coupling constants observed for **30** and **31** were 10.2 and 5.6 Hz respectively indicating that **30** carried its vicinal aryl groups in a *trans*-relationship while in **31**, the corresponding groups were *cis*-disposed.

Having established that phenyl-substituted cyclopropane **7** underwent fragmentation upon reaction with different aromatic aldehydes and ketones, we sought to explore the scope of this

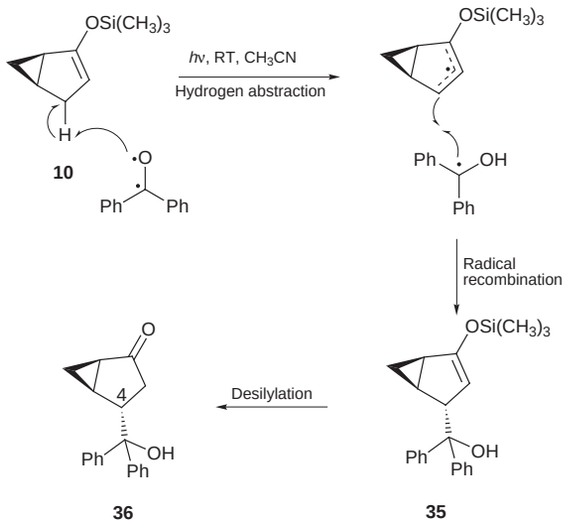
reaction in terms of the nature of the radical stabilising groups attached to the cyclopropyl ring. Specifically, we turned our attention to the evaluation of an ester as a radical stabilising group. Irradiation of benzaldehyde in the presence of the cyclopropyl ester **8** delivered small yields of two diastereoisomeric tetrahydrooxepin products **33** (8%) and **34** (8%) (Scheme 10). Again, the coupling constant between H_a and H_b



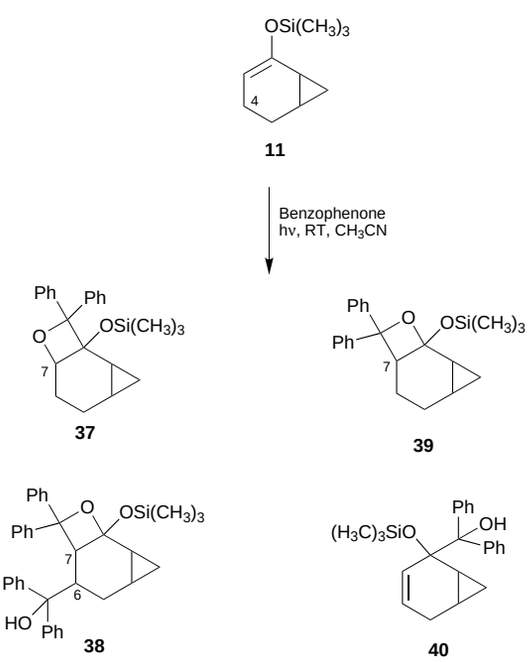
Scheme 10

was used for the assignment of the relative stereochemistry in **33** and **34** and a 10.5 Hz coupling for **33** and 2.7 Hz coupling for **34** indicated that these were respectively *trans*- and *cis*-diastereoisomers (ester group with respect to the phenyl group). Enol ether **8** was also reacted with benzophenone, 4-cyanobenzaldehyde and 4-methoxybenzaldehyde. Starting enol ether was recovered from these latter reactions.

Diphenyl cyclopropyl enol ether **9** failed to react with benzaldehyde, 4-cyanobenzaldehyde and 4-methoxybenzaldehyde and the starting enol ether **9** was recovered from these reactions. When enol ether **9** was irradiated in the presence of benzophenone, various high molecular weight compounds were observed by mass spectrometric examination. The ^1H and $\{^1H\}^{13}C$ NMR spectra were complex and structural assignment of the products of this reaction was not possible. The absence of any identifiable products may be a reflection of the fact that while cyclopropyl ring fragmentation in systems such as **9** may be rapid, the recombination of the derived 1,7-biradical intermediate may be slowed by unfavourable steric interactions in the transition state leading to the seven-membered ring product. Consequently, decomposition products tend to predominate over oxepane-containing materials.



Scheme 11



Scheme 12

Photoreactions of bicyclic cyclopropyl silyl enol ethers

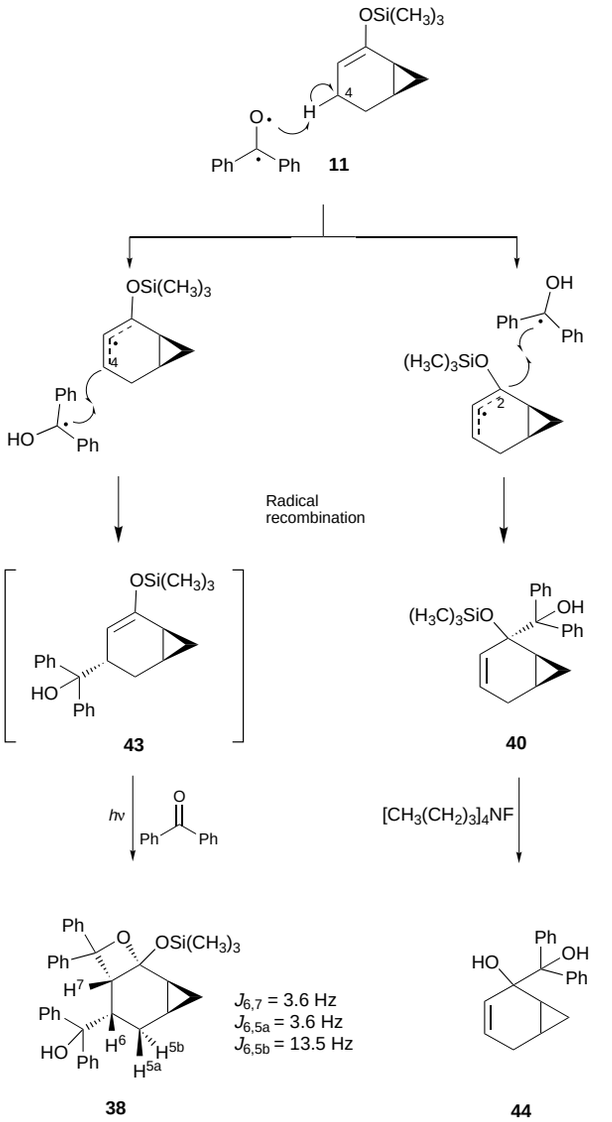
The five-membered ring enol ether **10** was photoreacted with benzophenone in acetonitrile using similar conditions to those described for the monocyclic systems. This reaction gave a complex mixture of products which, after repeated chromatography, yielded diphenylmethanol derivative **36** (9%). The remainder of the material isolated from this reaction consisted of either 1,1,2,2-tetraphenylethane-1,2-diol or unreacted starting enol ether.

A proposed mechanism for the formation of **36** is shown in Scheme 11 and involves initial allylic hydrogen atom abstraction by the photoexcited benzophenone triplet diradical. It is proposed that *exo*-face recombination with the diphenylmethanol radical gives silyl enol ether **35** which upon proteolytic desilylation delivers the ultimately observed product **36**. Similar processes have been previously observed by other workers.[27] It is interesting to note that in this bicyclic enol ether, no oxetane or oxepane products were observed and that the allylic hydrogen abstraction pathway is clearly the favoured reaction pathway.

Photoaddition of bicyclo[4.1.0]heptane enol ether **11** with benzophenone gave a mixture of compounds which were again isolated by repeated chromatography and were identified as **37** (1.5%), **39** (2%), **38** (0.6%) and **40** (6%) (Scheme 12).

Oxetanes **37** and **39** are clearly formed by conventional Paternò–Büchi reactions, with **37** being formed by initial photoaddition of the triplet oxygen radical to the less substituted carbon of the alkene and **39** by addition of the oxygen radical to the more hindered carbon of the alkene. It was not possible to determine the relative stereochemistry of C7 in **37** and **39** unequivocally but we propose, based on analogy to the 5-membered homologue **36**, that the cyclopropyl and oxetane rings of these compounds reside in a *trans*-relationship.

Compound **38** was presumably formed by allylic hydrogen atom abstraction at C4 of **11** followed by *exo*-face addition of the diphenylmethanol radical (Scheme 13). Another molecule of benzophenone then underwent photoaddition with enol ether **43** from the *exo*-face to form the 2-substituted oxetane product **38**. Once more, the mechanism for the formation of **40** is proposed to involve initial hydrogen abstraction at C4 of **11** by the photoexcited benzophenone triplet radical. The radical then undergoes allylic rearrangement to give a more stable α-oxy radical at C2. This is followed by radical recombination from the *exo*-face to generate **40**. The assignment of structure



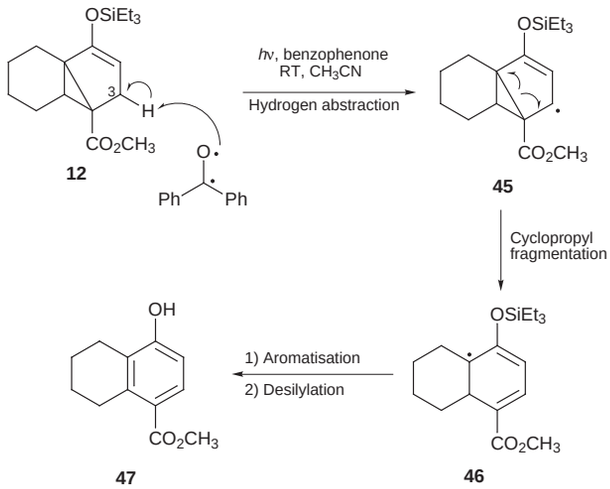
Scheme 13

40 was partly supported by subjection to reaction with tetrabutylammonium fluoride to give the corresponding diol **44** (16%).

Photoreactions of a tricyclic cyclopropyl silyl enol ether

Irradiation of the tricyclic enol ether **12** in the presence of benzophenone, followed by desilylation with tetrabutylammonium fluoride gave the tetrahydronaphthalene derivative **47** in 28% yield. This structure was confirmed by various spectroscopic techniques including X-ray analysis.[28] A mechanism has been proposed for the formation of this compound (Scheme 14). Once more, allylic hydrogen atom abstraction is invoked, generating allylic radical **45**. The cyclopropyl ring then undergoes fragmentation to give the radical intermediate **46** which upon oxidation followed by desilylation affords the tetrahydronaphthalene product **47**.

In summary, the photoreaction of monophenyl substituted silyl enol ether **7** with benzophenone, benzaldehyde and 4-methoxybenzaldehyde gives oxepane derivatives in a single step. Other monocyclic systems give mainly 3-substituted oxetane products. These results demonstrate that in order to generate a seven-membered oxepane ring, a stabilised but unencumbered radical, (*e.g.* **24**) must be produced by fragmentation of the cyclopropylmethyl radical intermediate. It is also observed that the bicyclic and tricyclic systems predominantly undergo H-abstraction at the allylic position in preference to cycloaddition/fragmentation reactions. The results from these con-



Scheme 14

formationally constrained systems indicate that apart from carrying suitable radical stabilising substituents, cyclopropyl enol ethers must be able to accommodate the stereoelectronic requirements of rapid cyclopropyl ring fragmentation. These studies have shown that the tandem Paternò–Büchi reactions of simple silyl enol ethers with suitable ketones or aldehydes may provide access to more complex oxygenated heterocycles.

Experimental

Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity 300 spectrometer or a JEOL GX-400 spectrometer, operating at 300 and 400 MHz for proton and 75 and 100 MHz for carbon respectively. Deuterochloroform ($CDCl_3$) was used as a solvent and the residual peak of chloroform ($CHCl_3$) was used as internal reference (δ 7.26) for proton while the central peak of $CDCl_3$ (δ 77.0) was used as reference for carbon spectra. Chemical shifts are quoted on the δ (ppm) scale followed by multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet), coupling constant(s) J (Hz), assignment (where possible) and integrated intensity (for proton spectra). Distortionless enhancement by polarisation transfer (DEPT), nuclear Overhauser effect (NOE) difference spectroscopy, cycled Overhauser effect difference spectroscopy (cyclonoe), homonuclear (^{1}H–^{1}H) correlation spectroscopy (COSY) and heteronuclear (^{1}H–^{13}C) correlation spectroscopy (HETCOSY) techniques were used in the assignment of NMR spectra.[29]

Melting point determinations were performed using a Kofler hot-stage and are uncorrected. Microanalyses were performed by the Microanalytical Unit of Research School of Chemistry, The Australian National University, Canberra, Australia.

Electronic spectra were recorded in chloroform or acetonitrile unless otherwise stated, using a Varian Super Scan 3 spectrophotometer and are listed as absorbance maxima (nm) followed by extinction coefficient ε (cm^{-1} M^{-1}).

Infrared spectra were recorded as potassium bromide discs for solids or as neat films between sodium chloride plates for liquids using a Perkin-Elmer 983G spectrophotometer or a Perkin-Elmer 1600 Series FTIR spectrophotometer.

High and low resolution mass spectra were recorded using a VG Micromass 7070F instrument using positive ion electron impact techniques at 70 eV. Ions of intensity greater than 20% are quoted as an *m*/*z* value followed by intensity (%).

Analytical thin layer chromatography (TLC) was conducted on aluminium-backed 0.2 mm thick silica gel 60 GF_{254} plates supplied by Merck and the chromatograms were visualised under a 254 nm UV lamp and/or with anisaldehyde–sulfuric acid–ethanol (2:5:93) dip reagent. Preparative thin layer chromatography (PLC) was carried out on 20 × 20 cm glass

plates coated with silica gel (Merck Kieselgel GF_{254}) and eluted with the solvent system indicated. The separated compounds were located under 254 nm UV light and extracted using diethyl ether or dichloromethane. Flash chromatography was carried out according to the method of Still *et al.*[30] using Merck Kieselgel 60G No. 7731 and eluted with the solvent system indicated.

Medium pressure liquid chromatography (MPLC) was conducted using a Büchi 681 pump, a Büchi 648 fraction collector and 'Plastiglass' columns packed with Merck Kieselgel 60G No. 7731, also supplied by Büchi. Normal-phase high pressure liquid chromatography (HPLC) was carried out with an EXSIL 100 5μ SiOH 250 × 10 mm column using HPLC quality or redistilled solvents as indicated and an ISCO Model 2350 pump connected to the column indicated. The peaks were detected using an ERMA ERC-7512 refractive index detector connected to a Spectra-Physics SP4270 integrator.

Materials

Many reagents were available from the Aldrich Chemical Company and were used as supplied. Drying agents and other inorganic salts were generally purchased from Ajax Chemicals. Solvents and reagents for the reactions were purified according to well established procedures.[31] Tetrahydrofuran (THF) and diethyl ether were purified by distillation from sodium benzophenone ketyl. All irradiation experiments were conducted using a medium pressure mercury lamp with a Pyrex filter in spectroscopic grade solvents.

Preparation of silyl enol ethers

1-Trimethylsilyloxy-1-cyclopropylethylene **4** was prepared as follows: butyllithium (14.3 ml, 35.7 mmol, 2.5 M solution in hexane) was added to a solution of diisopropylamine (5.0 ml, 35.7 mmol) in dry tetrahydrofuran (35 ml) at 0 °C under a nitrogen atmosphere. The solution was stirred for 15 min then cooled to −78 °C, followed by dropwise addition of cyclopropyl methyl ketone (2.0 g, 23.8 mmol) in dry tetrahydrofuran (0.4 ml). The reaction mixture was stirred for 30 min and chlorotrimethylsilane (7.0 ml, 54.7 mmol) was then added dropwise. The resulting solution was then stirred for a further 1 h, then warmed to 0 °C before pouring into a mixture of water (20 ml) and pentane (20 ml). The pentane extract was washed with water (2 × 10 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Distillation (39 °C/12 mmHg, lit.,[32] bp 38–40 °C/12 mmHg) gave enol ether **4** as a colourless oil (3.49 g, 94%); δ_H($CDCl_3$, 300 MHz) 0.19 (s, 9H), 0.55 (m, 4H), 1.40 (m, 1H), 3.99 (s, 1H), 4.13 (s, 1H); δ_C($CDCl_3$, 75 MHz) 0.0, 4.4, 15.5, 87.6, 159.1; ν_{max}/cm^{-1} 3093, 2960, 1648, 1443, 1253, 1082, 1011, 847; *m*/*z* 156 ($M^{+\bullet}$, 29%), 147 (40), 141 (76), 131 (21), 99 (43), 75 (73), 73 (100), 59 (24), 57 (52), 56 (36), 55 (75).

Silyl enol ethers **5**–**11** were prepared in a similar manner and their physical properties are given below.

[1-(2-Methylcyclopropyl)vinyloxy]trimethylsilane 5. Prepared from 1-(2-methylcyclopropyl)ethanone. Oil, bp 73 °C/760 mmHg, 79%; δ_H($CDCl_3$, 300 MHz) 0.18 (s, 9H), 0.32 (m, 1H), 0.75 (m, 1H), 1.00 (m, 1H), 1.04 (s, 3H), 1.10 (m, 1H), 3.96 (s, 1H), 4.08 (s, 1H); δ_C($CDCl_3$, 75 MHz) 0.1, 12.7, 12.9, 18.3, 24.3, 87.2, 150.0; ν_{max}/cm^{-1} 3078, 3002, 2957, 1645, 1403, 1253; *m*/*z* 171 ($M^{+\bullet}$ + 1, 33%), 91 (26), 73 (100), 69 (23), 57 (25), 55 (23).

[1-(2,2-Dimethylcyclopropyl)vinyloxy]trimethylsilane 6. Prepared from 1-(2,2-dimethylcyclopropyl)ethanone.[33] Oil, bp 85 °C/760 mmHg, 58%; δ_H($CDCl_3$, 300 MHz) 0.20 (s, 9H), 0.53 (d, *J* 7.0, 2H), 1.07 (s, 3H), 1.09 (s, 3H), 1.22 (t, *J* 7.0, 1H), 4.02 (s, 1H), 4.12 (s, 1H); δ_C($CDCl_3$, 75 MHz) 0.2, 18.5, 19.4, 27.1, 29.9, 90.2, 158.1, C2 not observed; ν_{max}/cm^{-1} 3068, 2957, 1634, 1307, 1253; *m*/*z* 184 ($M^{+\bullet}$, 21%), 169 (26), 147 (23), 141 (75), 84 (27), 79 (41), 75 (65), 73 (100), 57 (23), 55 (30) (HRMS: $C_{10}H_{20}OSi$ requires $M^{+\bullet}$, 184.1283. Found: M^+, 184.1281).

[1-(2-Phenylcyclopropyl)vinyloxy]trimethylsilane 7. Prepared from 1-(2-phenylcyclopropyl)ethanone.[34] Oil, bp 95 °C/0.7 mmHg, 65%; δ_H($CDCl_3$, 400 MHz) 0.23 (s, 9H), 1.03 (m, 1H), 1.28 (m, 1H), 1.67 (m, 1H), 2.13 (m, 1H), 4.07 (s, 1H), 4.18 (s, 1H), 7.00–7.30 (m, 5H); δ_C($CDCl_3$, 100 MHz) 0.1, 14.1, 22.4, 27.9, 88.5, 125.5, 125.9, 128.3, 142.4, 157.5; ν_{max}/cm^{-1} 3062, 3029, 2959, 1645, 1498, 1316, 1288; *m*/*z* 233 ($M^{+\bullet}$ + 1, 39%), 145 (51), 143 (45), 117 (39), 115 (30), 91 (40), 73 (100) (HRMS: $C_{14}H_{20}OSi$ requires $M^{+\bullet}$, 232.1283. Found: M^+, 232.0964).

[2-(1-Trimethylsilyloxyvinyl)cyclopropane]carboxylic acid ethyl ester 8. Prepared from (2-acetylcyclopropane)carboxylic acid ethyl ester **14**. Oil, bp 75 °C/0.15 mmHg, 31%; δ_H($CDCl_3$, 300 MHz) 0.19 (s, 9H), 1.18 (m, 2H), 1.26 (t, *J* 7, 3H), 1.81 (m, 1H), 2.02 (m, 1H), 4.07 (d, *J* 1.2, 1H), 4.13 (q, *J* 7, 2H), 4.22 (d, *J* 1.2, 1H); δ_C($CDCl_3$, 75 MHz) −0.1, 12.9, 14.2, 19.4, 26.2, 60.5, 89.6, 155.3, 173.7; ν_{max}/cm^{-1} 2962, 1728, 1627, 1255, 1179; *m*/*z* 228 ($M^{+\bullet}$, 74%), 213 (27), 199 (26), 185 (36), 183 (68), 156 (39), 155 (100), 141 (64), 111 (25), 110 (55), 103 (66), 82 (43), 75 (91), 73 (100), 57 (21), 55 (22).

[1-(2,2-Diphenylcyclopropyl)vinyloxy]trimethylsilane 9. Prepared from 1-(2,2-diphenylcyclopropyl)ethanone **17**. Oil, 183 °C/0.8 mmHg, 93%; δ_H($CDCl_3$, 300 MHz) −0.03 (s, 9H), 1.43 (dd, *J* 9.0, 4.6, 1H), 1.87 (dd, *J* 6.2, 4.6, 1H), 2.34 (dd, *J* 9.0, 6.2, 1H), 3.98 (s, 1H), 4.18 (s, 1H), 7.13–7.50 (m, 10H); δ_C($CDCl_3$, 75 MHz) −0.5, 18.5 (CH_2), 32.0, 36.7, 89.5, 125.7, 126.1, 127.5, 127.9, 128.2, 130.2, 141.5, 146.9, 155.7; ν_{max}/cm^{-1} 3026, 2964, 1600, 1496, 1447, 1253; *m*/*z* 308 ($M^{+\bullet}$, 52%), 219 (32), 218 (61), 217 (90), 203 (42), 202 (29), 194 (23), 193 (59), 192 (29), 191 (32), 189 (20), 183 (27), 179 (32), 178 (47), 165 (76), 141 (42), 118 (20), 117 (95), 115 (81), 91 (69), 77 (25), 75 (73), 74 (35), 73 (100).

(Bicyclo[3.1.0]hex-2-en-2-yloxy)trimethylsilane 10. Prepared from bicyclo[3.1.0]hexan-2-one.[35] Oil, 61%; δ_H($CDCl_3$, 300 MHz) 0.22 (s, 9H), 1.05 (m, 2H), 1.59 (m, 2H), 2.22 (d, *J* 12.0, 1H), 2.49 (dd, *J* 12.0, 5.1, 1H), 4.22 (s, 1H); δ_C($CDCl_3$, 75 MHz) 0.0, 13.9, 15.1, 22.7, 31.1, 97.6, 158.5; ν_{max}/cm^{-1} 2957, 2915, 1654, 1394, 1251; *m*/*z* 169 ($M^{+\bullet}$ + 1, 58%), 75 (28), 73 (100).

(Bicyclo[4.1.0]hept-2-en-2-yloxy)trimethylsilane 11. Prepared from bicyclo[4.1.0]heptan-2-one.[36] Oil, bp 75 °C/4.5 mmHg, 86%; δ_H($CDCl_3$, 300 MHz) 0.18 (s, 9H), 0.60–0.78 (m, 2H), 1.09 (m, 1H), 1.35 (m, 1H), 1.52 (m, 1H), 1.65–1.99 (m, 3H), 4.58 (dt, *J* 6.9, 1.8, H3, 1H); δ_C($CDCl_3$, 75 MHz) 0.2, 8.9, 13.8, 14.8, 18.8, 19.1, 98.0, 152.3; ν_{max}/cm^{-1} 3004, 2957, 2917, 1395, 1251; *m*/*z* 182 ($M^{+\bullet}$, 11%), 149 (20), 74 (41), 73 (100), 72 (24), 57 (32), 55 (30) (HRMS: $C_{10}H_{18}OSi$ requires $M^{+\bullet}$, 182.1127. Found: M^+, 182.1075).

(2-Acetylcyclopropane)carboxylic acid ethyl ester 14

A solution of ethyl diazoacetate (2 ml, 19.0 mmol) in benzene (16 ml) was added to a mixture of methyl vinyl ketone (2 ml, 24 mmol) and palladium(II) acetate (42 mg) in benzene (10 ml) at a rate of 7 mmol h^{-1} while the temperature of the reaction mixture was maintained at 40 °C. After half of the ethyl diazoacetate was introduced, another portion of palladium(II) acetate (42 mg) was added. Upon completion of addition (3 h), the reaction mixture was cooled and washed with saturated aqueous sodium carbonate (3 × 10 ml) and water (2 × 5 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. Distillation (80 °C/0.3 mmHg, lit.,[23] bp 115–125 °C/15 mmHg) yielded the title compound **14** (1.52 g, 51%) as a colourless liquid; δ_H($CDCl_3$, 300 MHz) 1.24 (t, *J* 7, 3H), 1.39 (m, 2H), 2.23 (m, 1H), 2.27 (s, 3H), 2.45 (m, 1H), 4.12 (q, *J* 7, 2H); δ_C($CDCl_3$, 75 MHz) 14.1, 17.0, 24.1, 29.5, 30.7, 61.0, 171.9, 205.2; ν_{max}/cm^{-1} 3000, 1740, 1714, 1343, 1200; *m*/*z* 156 ($M^{+\bullet}$, 1%), 91 (29), 90 (20), 75 (24), 61 (25), 57 (100).

1-(2,2-Diphenylcyclopropyl)ethanone 17

A solution of ethyl diazoacetate in 1,1-diphenylethylene (4 ml) was added to 1,1-diphenylethylene (25.5 ml) at 160–165 °C over a period of 6 h. After addition, the reaction mixture was cooled and a solution of potassium hydroxide (1.6 g) in ethanol (20 ml) was added. The reaction was heated at reflux for another 1 h.

Upon cooling, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in water (100 ml) and 2 M sodium hydroxide (20 ml). The aqueous layer was extracted with diethyl ether (2 × 100 ml) and then acidified using 2 M hydrochloric acid. The solid formed was filtered and recrystallised from methanol–water to give carboxylic acid **16** (3.71 g, 60%) as a white solid, mp 169–171 °C (lit.,[24] mp 170–171 °C); δ_H($CDCl_3$, 300 MHz) 1.66 (dd, *J* 8.1, 5.0, 1H), 2.11 (dd, *J* 6.0, 5.0, 1H), 2.49 (dd, *J* 8.1, 6.0, 1H), 7.17–7.38 (m, 10H), OH not observed; δ_C($CDCl_3$, 75 MHz) 20.7, 28.6, 41.1, 126.7, 127.1, 127.6, 128.4, 128.5, 129.6, 139.8, 144.6, 176.7; ν_{max}/cm^{-1} 3576, 3026, 1703, 1600, 1495, 1447, 1254; *m*/*z* 238 ($M^{+\bullet}$, 40%), 193 (74), 192 (34), 191 (21), 178 (29), 165 (25), 115 (31), 91 (32), 58 (31).

A solution of **16** (2.0 g, 8.4 mmol) in diethyl ether (63 ml) was added to a solution of methyllithium (18 ml, 1.4 M in diethyl ether) in diethyl ether (66 ml) over a period of 20 min under a nitrogen atmosphere. The reaction mixture was stirred for a further 20 min and poured into aqueous ammonium chloride (2.1 g in 105 ml water). The organic layer was washed with saturated aqueous sodium chloride until the washings were pH neutral to litmus. It was then dried ($MgSO_4$), filtered and concentrated under reduced pressure. Distillation (170 °C/0.8 mmHg, lit.,[25] bp 159–160 °C/2.5 mmHg) gave ketone **17** (1.98 g, 88%) as a colourless oil; δ_H($CDCl_3$, 300 MHz) 1.64 (dd, *J* 7.8, 4.5, 1H), 2.21 (s, 3H), 2.34 (dd, *J* 6.3, 4.5, 1H), 2.88 (dd, *J* 7.8, 6.3, 1H), 7.18–7.52 (m, 10H); δ_C($CDCl_3$, 75 MHz) 20.9, 31.1, 37.1, 42.6, 126.5, 126.9, 127.4, 128.3, 128.4, 129.8, 139.3, 144.9, 203.7; ν_{max}/cm^{-1} 3027, 1702, 1602, 1496, 1446, 1273; *m*/*z* 236 ($M^{+\bullet}$, 22%), 193 (85), 178 (35), 165 (43), 115 (100), 91 (35), 83 (24).

Methyl 2-triethylsilyloxytricyclo[4.4.0.0^{1,5}]dec-2-ene-5-carboxylate 12

Potassium hydride (254 mg, 1.4 mmol, 20–22% dispersion in mineral oil) was washed with freshly distilled light petroleum (bp 40–60 °C) (5 × 5 ml) and dried under vacuum. 1,4-Dioxane (5 ml), methyl 2-oxotricyclo[4.4.0.0^{1,5}]decane-5-carboxylate[22] **13** (200 mg, 0.96 mmol) and chlorotriethylsilane (218 μl, 1.3 mmol) were added and the resulting suspension was heated at reflux for 24 h. The cooled mixture was quenched with saturated aqueous sodium hydrogen carbonate (5 ml) and extracted with diethyl ether (3 × 3 ml). The combined diethyl ether extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography using light petroleum (bp 60–80 °C)–diethyl ether (10:1) gave **12** (R_f 0.81) (84.3 mg, 27%) as a light yellow oil; δ_H($CDCl_3$, 400 MHz) 0.68 (q, *J* 10.6, 6H), 0.98 (t, *J* 10.6, 9H), 1.18–1.50 (m, 5H), 1.58–1.73 (m, 2H), 1.89 (m, 1H), 2.17 (m, 1H), 2.37 (dd, *J* 21.8, 2.8, 1H), 2.77 (dd, *J* 21.8, 2.8, 1H), 3.70 (s, 3H), 4.21 (t, *J* 2.8, 1H); δ_C($CDCl_3$, 100 MHz) 4.7, 6.6, 18.0, 19.9, 20.9, 21.1, 33.3, 34.1, 35.5, 38.9, 51.4, 95.0, 159.0, 172.4; ν_{max}/cm^{-1} 2929, 1224, 1108; *m*/*z* 322 ($M^{+\bullet}$, 100%), 321 (21), 293 (51), 291 (29), 264 (21), 263 (80), 233 (33), 159 (52), 131 (24), 117 (21), 115 (37), 103 (27), 87 (77), 75 (27), 59 (69) (HRMS: $C_{18}H_{30}O_3Si$ requires $M^{+\bullet}$, 322.1964. Found: M^+, 322.1966).

Photoreactions of cyclopropyl silyl enol ethers

3-Cyclopropyl-2,2-diphenyl-3-(trimethylsilyloxy)oxetane 19. A solution of **4** (37 mg, 0.24 mmol) and benzophenone (52 mg, 0.28 mmol) in acetonitrile (2.5 ml) was degassed and irradiated at −25 °C for 1 day using a medium pressure mercury lamp. The reaction mixture was concentrated and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 60–80 °C)–diethyl ether (4:1) to give oxetane **19** as a white crystalline solid (R_f 0.7) (59 mg, 73%), mp 67–68 °C. The product **19** was further recrystallised from light petroleum (bp 40–60 °C) at −25 °C for microanalysis; δ_H($CDCl_3$, 300 MHz) −0.15 (s, 9H), 0.20–0.58 (m, 4H), 1.05 (m, 1H), 4.31 (d, *J* 6.2, 1H), 4.56 (d, *J* 6.2, 1H), 7.11–7.62 (m, 10H); δ_C($CDCl_3$, 75 MHz) 1.2, 1.7, 1.8, 17.8, 76.7, 80.2, 87.5, 124.9, 126.2, 126.3, 126.5, 127.5, 127.6, 142.9, 144.1; ν_{max}/cm^{-1} 3087, 3022, 2950, 1589, 1449, 1380; *m*/*z* 308 ($M^{+\bullet}$ − CH_2O, 14%), 156 (68), 141 (100), 77 (20), 75 (68), 73 (92); λ_{max}(CH_3CN)/nm 250.0, 224 (sh), 206 nm (log ε 5.41, 6.52, 6.61) (Found: C, 74.2; H, 7.8. $C_{21}H_{26}O_2Si$ requires C, 74.5; H, 7.7%).

4-(3-Cyclopropyl-3-trimethylsilyloxyoxetan-2-yl)benzonitrile 20. A mixture of **4** (89 mg, 0.57 mmol), 4-cyanobenzaldehyde (50 mg, 0.38 mmol) and sodium carbonate (5 mg) in benzene (4.3 ml) was degassed and irradiated at 25 °C for 23 h using a medium pressure mercury lamp. The reaction mixture was concentrated and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 40–60 °C)–diethyl ether (2:1). The major band was isolated to give **20** as a colourless oil (R_f 0.63) (50 mg, 46%); δ_H($CDCl_3$, 400 MHz) −0.16 (s, 9H), 0.50–0.72 (m, 4H), 1.36 (m, 1H), 4.43 (d, *J* 5.0, 1H), 4.52 (d, *J* 5.0, 1H), 5.49 (s, 1H), 7.42 (d, *J* 6.0, 2H), 7.66 (d, *J* 6.0, 2H); δ_C($CDCl_3$, 100 MHz) 1.4, 1.9, 2.0, 18.7, 78.1, 80.0, 92.0, 110.0, 119.0, 127.1, 131.5, 144.1; ν_{max}/cm^{-1} 3083, 3009, 2959, 2229, 1610, 1504, 1378, 1253; *m*/*z* 287 ($M^{+\bullet}$, 3%), 157 (23), 156 (27), 141 (32), 130 (37), 91 (35), 75 (45), 73 (90), 58 (100), 51 (25); λ_{max}(CH_3CN)/nm 235 nm (log ε 7.23) (HRMS: $C_{16}H_{21}NO_2Si$ requires $M^{+\bullet}$, 287.1341. Found: M^+, 287.1328).

[3-(2-Methylcyclopropyl)-2,2-diphenyloxetan-3-yloxy]-trimethylsilane 21. A solution of **5** (200 mg, 1.18 mmol) and benzophenone (236 mg, 1.29 mmol) in acetonitrile (12.3 ml) was degassed and irradiated at 25 °C for 48 h using a medium pressure mercury lamp. The reaction mixture was concentrated and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 40–60 °C)–diethyl ether (8:1). The major band was isolated to give an equimolar mixture of two inseparable diastereoisomeric oxetanes **21** (R_f 0.73) as a white crystalline solid (104.4 mg, 25%), mp 65–68 °C; δ_H($CDCl_3$, 300 MHz) (−0.17, −0.07) (s, 9H), (0.04, 0.25) (m, 1H), 0.51 (m, 2H), (0.62, 0.86) (m, 1H), (0.78, 0.80) (s, 3H), (4.01, 4.38) (d, *J* 6.3, 1H), (4.45, 4.61) (d, *J* 6.3, 1H), 7.18–7.71 (m, 10H); δ_C($CDCl_3$ 75 MHz) (1.1, 1.3), (8.8, 10.6), (9.2, 10.8), (17.5, 17.8), (26.4, 26.5), (75.1, 77.5), (80.5, 80.7), (97.4, 97.5), (124.7, 125.0), (126.1, 126.5), (126.3, 126.4), (127.4, 127.5), (127.6, 127.7), (142.8, 143.0), 144.2; ν_{max}/cm^{-1} 3059, 2998, 2956, 1597, 1449, 1253; *m*/*z* 322 ($M^{+\bullet}$ − CH_2O, 38%), 293 (29), 255 (26), 171 (36), 170 (100), 156 (20), 155 (64), 142 (25), 141 (74), 114 (21), 105 (41), 80 (20), 77 (38), 75 (63), 74 (21), 73 (97); λ_{max}(CH_3CN)/nm 250, 220 (sh), 205 nm (log ε 5.09, 6.89, 6.95) (Found: C, 75.0; H, 8.3. $C_{22}H_{28}O_2Si$ requires C, 75.0; H, 8.0%).

[3-(2,2-Dimethylcyclopropyl)-2,2-diphenyloxetan-3-yloxy]-trimethylsilane 22. A solution of **6** (200 mg, 1.09 mmol) and benzophenone (199 mg, 1.09 mmol) in acetonitrile (11.3 ml) was degassed and irradiated at 25 °C for 24 h using a medium pressure mercury lamp. The reaction mixture was then concentrated under reduced pressure and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 40–60 °C)–diethyl ether (8:1). The major product was identified to be oxetane **22** (R_f 0.73) as a white solid (40 mg, 10%), mp 57–58 °C; δ_H($CDCl_3$, 300 MHz) (−0.20, −0.14) (s, 9H), 0.28 (d, *J* 7.8, 1H), (0.42, 0.63) (s, 3H), (0.44, 0.88) (m, 1H), 0.98 (t, *J* 7.5, 1H), (1.02, 1.17) (s, 3H), (4.41, 4.47) (d, *J* 6.6, 1H), (4.50, 4.62) (d, *J* 6.6, 1H), 7.15–7.65 (m, 10H); δ_C($CDCl_3$, 75 MHz) (1.1, 1.6), (15.2, 17.2), (16.4, 18.0), (19.3, 19.6), (27.6, 28.8), (31.9, 32.3), (76.4, 79.6), (82.1, 82.2), (97.5, 98.1), (125.0, 126.4), (126.0, 126.2), (126.5, 126.6), 127, (127.4, 127.7), (127.4, 127.6), (142.5, 143.3), (143.6, 144.4); ν_{max}/cm^{-1} 3058, 2953, 1654, 1489, 1448; *m*/*z* 336 ($M^{+\bullet}$ − CH_2O, 9%), 184 (35), 169 (26), 141 (100), 105 (20), 74 (24), 73 (61); λ_{max}(CH_3CN)/nm 250, 220 (sh), 205 nm (log ε 5.25, 6.68, 6.76) (Found: C, 75.2; H, 8.6. $C_{22}H_{28}O_2Si$ requires C, 75.4; H, 8.3%).

(4,4,5,8,8-Pentaphenyl-3,9-dioxabicyclo[5.2.0]nonan-1-yloxy)-trimethylsilane 26. A solution of **7** (300 mg, 1.29 mmol) and benzophenone (282 mg, 1.55 mmol) in acetonitrile (13.5 ml)

was degassed and irradiated at 25 °C for 2.5 days using a medium pressure mercury lamp. The reaction mixture was concentrated. The resulting residue was subjected twice to preparative thin layer chromatography using light petroleum (60–80 °C)–ethyl acetate (9:1). The high R_f component was isolated to give a colourless oil **26** (R_f 0.59) (119 mg, 15%); δ_H($CDCl_3$, 300 MHz) 0.08 (s, 9H), 1.83 (m, 1H), 1.96 (t, *J* 13.6, 1H), 3.23 (dd, *J* 12.5, 6.2, 1H), 3.74 (d, *J* 12.9, 1H), 3.80 (d, *J* 12.9, 1H), 4.28 (d, *J* 15.4, 1H), 6.77–7.41 (m, 25H); δ_C($CDCl_3$, 75 MHz) 1.5, 31.9, 50.3, 71.1, 83.4, 86.6, 103.5, 125.1, 125.4, 125.6, 125.7, 126.5, 126.6, 127.1, 127.2, 127.6, 127.7, 128.3, 130.8, 139.8, 142.8, 144.1, 146.7, 146.9; ν_{max}/cm^{-1} 3058, 3024, 2954, 1599, 1493, 1447, 1264; *m*/*z* 596 ($M^{+\bullet}$, 0.78%), 399 (29), 313 (32), 297 (52), 282 (24), 270 (27), 256 (20), 255 (21), 232 (69), 207 (48), 193 (50), 167 (68), 115 (22), 105 (30), 91 (24), 75 (33), 73 (100), 58 (38); λ_{max}(CH_3CN)/nm 258 (log ε 6.24) (HRMS: $C_{40}H_{40}O_3Si$ requires $M^{+\bullet}$, 596.2747. Found: M^+, 596.2750).

(6*R,7*S**)-(6,7-Diphenyl-2,5,6,7-tetrahydrooxepin-3-yloxy)-trimethylsilane 29 and (6*R**,7*S**)-6,7-diphenyloxepan-3-one 32.** A solution of **7** (98 mg, 0.43 mmol), benzaldehyde (29 µl, 0.29 mmol) and sodium carbonate (5 mg) in benzene (3.0 ml) were degassed and irradiated at 25 °C for 17.5 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the residue was purified using HPLC [light petroleum (40–60 °C)–diethyl ether elution, 10:1, 3.0 ml min^{-1}] to afford a colourless oil **29** (t_R 6.0 min) (26 mg, 27%) and ketone **32** as a white crystalline solid (t_R 24.7 min) (5 mg, 6%), mp 99–100 °C.

For **29**: δ_H($CDCl_3$, 300 MHz) 0.25 (s, 9H), 2.38 (m, 1H), 2.88 (m, 1H), 3.22 (dt, *J* 10.5, 5.2, 1H), 4.13 (d, *J* 16.0, 1H), 4.42 (d, *J* 16.0, 1H) 4.86 (d, *J* 10.2, 1H), 5.17 (t, *J* 6.7, 1H), 7.05–7.21 (m, 10H); δ_C($CDCl_3$, 75 MHz) 0.3, 28.8, 53.6, 71.9, 86.9, 104.9, 125.9, 126.3, 126.6, 126.9, 127.3, 127.6, 127.8, 127.9, 128.2, 128.9, 141.5, 143.7, 151.0; ν_{max}/cm^{-1} 3062, 3031, 2959, 1666, 1494, 1452, 1382, 1253; *m*/*z* 338 ($M^{+\bullet}$, 6%), 233 (22), 232 (100), 180 (22), 142 (24), 141 (61), 75 (22), 73 (52); λ_{max}(CH_3CN)/nm 257 (log ε 5.96) (HRMS: $C_{21}H_{26}O_2Si$ requires $M^{+\bullet}$, 388.1702. Found: M^+, 388.1709).

For **32**: δ_H($CDCl_3$, 300 MHz) 2.00–2.20 (m, 2H), 2.63 (ddd, *J* 12.5, 7.5, 1.6, 1H), 3.24 (m, 2H), 4.22 (d, *J* 18.5, 1H), 4.37 (d, *J* 10.2, 1H), 4.45 (d, *J* 18.5, 1H), 6.88–7.15 (m, 10H); δ_C($CDCl_3$, 75 MHz) 31.1, 41.9, 55.4, 77.7, 92.2, 126.5, 126.6, 127.5, 127.8, 127.9, 128.3, 141.6, 141.7, 218.5; ν_{max}/cm^{-1} 3062, 3031, 2925, 1716, 1603, 1453, 1331, 1252; *m*/*z* 266 ($M^{+\bullet}$, 2.6%), 160 (100), 117 (29), 104 (85), 91 (24); λ_{max}(CH_3CN)/nm 255.5 (log ε 6.98) (HRMS: $C_{18}H_{18}O_2$ requires $M^{+\bullet}$, 266.1307. Found: M^+, 266.1304).

[(6*R,7*S**)-7-(4-Methoxyphenyl)-6-phenyl-2,5,6,7-tetrahydrooxepin-3-yloxy]trimethylsilane 30 and [(6*R**,7*R**)-7-(4-methoxyphenyl)-6-phenyl-2,5,6,7-tetrahydrooxepin-3-yloxy]-trimethylsilane 31.** A solution of **7** (72 mg, 0.31 mmol), 4-methoxybenzaldehyde (36 µl, 0.29 mmol) and sodium carbonate (5 mg) in benzene (3 ml) were degassed and irradiated at 25 °C for 24 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the resulting residue was purified using HPLC [light petroleum (bp 40–60 °C)–diethyl ether elution, 5:1, 2.5 ml min^{-1}] to afford a colourless oil **30** (t_R 7.6 min) (43 mg, 40%) and enol ether **31** as a colourless oil (t_R 7.8 min) (13 mg, 12%).

For **30**: δ_H($CDCl_3$, 300 MHz) 0.24 (s, 9H), 2.42 (m, 1H), 2.82 (m, 1H), 3.33 (dt, *J* 10.2, 5.1, 1H), 3.74 (s, 3H), 4.08 (d, *J* 16.2, 1H), 4.38 (d, *J* 16.2, 1H), 4.68 (d, *J* 10.2, 1H), 5.16 (t, *J* 6.7, 1H), 6.72–7.21 (m, 9H); δ_C($CDCl_3$, 75 MHz) 0.4, 28.9, 53.3, 55.2, 71.2, 86.3, 105.1, 113.4, 126.3, 127.9, 128.2, 128.3, 133.6, 143.9, 151.1, 158.8; ν_{max}/cm^{-1} 3030, 2958, 1666, 1612, 1513, 1453, 1251; *m*/*z* 368 ($M^{+\bullet}$, 3%), 233 (44), 232 (100), 231 (57), 217 (20), 210 (29), 209 (33), 143 (32), 142 (53), 141 (78), 121 (21), 115 (20), 75 (37), 73 (55); λ_{max}(CH_3CN)/nm 280, 270, 221 (log ε 6.30, 6.35, 7.18) (HRMS: $C_{22}H_{28}O_3Si$ requires $M^{+\bullet}$, 368.1808. Found: M^+, 368.1804).

For **31**: δ_H($CDCl_3$, 400 MHz) 0.24 (s, 9H), 2.17 (ddd, *J* 15.9, 7.7, 2.8, 1H), 2.84 (m, 1H), 3.58 (m, 1H), 3.71 (s, 3H), 4.36 (m, 2H), 4.93 (d, *J* 5.6, 1H), 5.08 (ddd, *J* 7.6, 4.1, 1.6, 1H), 6.61–7.20 (m, 9H); δ_C($CDCl_3$, 75 MHz) 0.3, 27.1, 50.8, 55.1, 71.5, 84.5, 106.5, 112.7, 125.9, 127.6, 127.8, 128.9, 132.4, 142.0, 151.8, 158.3; ν_{max}/cm^{-1} 3030, 3001, 2958, 1666, 1612, 1513, 1453, 1251; *m*/*z* 368 ($M^{+\bullet}$, 3%), 233 (22), 232 (100), 231 (29), 142 (26), 141 (71), 75 (20), 73 (39); λ_{max}(CH_3CN)/nm 279, 273, 219.5 (sh), 208 (log ε 6.16, 6.23, 7.15, 7.33) (HRMS: $C_{22}H_{28}O_3Si$ requires $M^{+\bullet}$, 368.1808. Found: M^+, 368.1811).

(2*R,3*S**)-2-Phenyl-6-trimethylsilyloxy-2,3,4,7-tetrahydrooxepine-3-carboxylic acid ethyl ester 33 and (2*R**,3*R**)-2-phenyl-6-trimethylsilyloxy-2,3,4,7-tetrahydrooxepine-3-carboxylic acid ethyl ester 34.** A solution of **8** (50 mg, 0.22 mmol), benzaldehyde (38 µl, 0.33 mmol) and sodium carbonate (5 mg) in benzene (2.3 ml) were degassed and irradiated at 25 °C for 24.5 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the resulting residue was purified using HPLC [light petroleum (bp 40–60 °C)–diethyl ether elution, 6:1, 2 ml min^{-1}] to afford a colourless oil **33** (t_R 10.0 min) (6 mg, 8%) and enol ether **34** as a colourless oil (t_R 11.0 min) (6 mg, 8%).

For **33**: δ_H($CDCl_3$, 300 MHz) 0.13 (s, 9H), 1.17 (t, *J* 7.2, 3H), 2.16 (m, 1H), 2.80 (m, 2H), 3.54 (d, *J* 10.5, 1H), 3.78 (m, 2H), 4.07 (q, *J* 7.2, 2H), 4.96 (dm, *J* 6.6, 1H), 7.21–7.67 (m, 5H); δ_C($CDCl_3$, 75 MHz) 0.1, 13.9, 24.9, 53.8, 60.4, 65.7, 80.1, 96.1, 126.5, 127.3, 128.0, (3 × C) not observed; ν_{max}/cm^{-1} 2984, 1729, 1675, 1445, 1253.

For **34**: δ_H($CDCl_3$, 300 MHz) 0.19 (s, 9H), 1.26 (t, *J* 7.1, 3H), 238 (m, 3H), 4.14 (q, *J* 7.1, 2H), 4.21 (m, 2H), 4.67 (d, *J* 2.9, 1H), 4.91 (m, 1H), 7.20–7.63 (m, 5H); δ_C($CDCl_3$, 75 MHz) 0.5, 14.2, 20.8, 34.0, 60.2, 69.7, 82.9, 110.2, 125.5, 128.0, 128.4, (3 × C) not observed; ν_{max}/cm^{-1} 2960, 1737, 1692, 1253.

[1-Hydroxy-1,1-(4-diphenyl)methyl]bicyclo[3.1.0]hexan-2-one 36. A solution of **10** (60 mg, 0.36 mmol) and benzophenone (78 mg, 0.43 mmol) in acetonitrile (5 ml) was degassed and irradiated at 25 °C for 30 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 60–80 °C)–diethyl ether (4:1) as eluent. The major band was isolated to give a white crystalline solid **36** (t_R 0.03) (9 mg, 9%), mp 180–181 °C; δ_H($CDCl_3$, 300 MHz) 0.96 (q, *J* 4.8, 1H), 1.15 (m, 1H), 1.84 (m, 1H), 1.92 (m, 1H), 2.17 (d, *J* 7.6, 1H), 2.22 (d, *J* 8.4, 1H), 2.27 (s, 1H), 3.49 (dd, *J* 8.2, 1.4, 1H), 7.18–7.56 (m, 10H); ν_{max}/cm^{-1} 3400, 3031, 2915, 2894, 1704; *m*/*z* 279 ($M^{+\bullet}$, 3%), 205 (27), 183 (100), 105 (90), 77 (57); λ_{max}(CH_3CN)/nm 210, 205 (log ε 6.55, 6.68) (HRMS: $C_{19}H_{18}O_2$ requires $M^{+\bullet}$, 278.1307. Found: M^+, 278.1309).

6,7,7-Triphenyloxepan-3-one 28

To a solution of **26** (23 mg, 0.04 mmol) and 3 Å molecular sieves (10 mg) in dry dichloromethane (1 ml) at 0 °C was added tetrabutylammonium fluoride (44 µl, 1 M in THF). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting solution was diluted with water (1 ml) and extracted with dichloromethane (3 × 1 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified using HPLC [light petroleum (bp 40–60 °C)–diethyl ether elution, 6:1, 2.0 ml min^{-1}] to afford a white crystalline solid **28** (t_R 17.0 min) (11 mg, 82%), mp 164–165 °C and benzophenone (t_R 11.0 min) (5 mg, 70%); δ_H($CDCl_3$, 300 MHz) 2.30 (m, 3H), 3.02 (m, 1H), 4.10 (d, *J* 17.9, 1H), 4.18 (d, *J* 17.9, 1H), 4.35 (dd, *J* 6.3, 3.0, 1H), 7.00–7.56 (m, 15H); δ_C($CDCl_3$, 75 MHz) 26.7, 37.9, 49.5, 71.7, 87.5, 126.2, 126.3, 126.8, 127.2, 127.6, 127.7, 128.3, 128.6, 130.3, 140.9, 142.4, 145.5, 213.7; ν_{max}/cm^{-1} 3056, 2928, 1712, 1598, 1493, 1265; *m*/*z* 342 ($M^{+\bullet}$, 0.4%), 162 (23), 161 (100), 117 (22), 105 (30), 104 (27); λ_{max}(CH_3CN)/nm 257 (log ε 6.11) (HRMS: $C_{24}H_{22}O_2$ requires $M^{+\bullet}$, 342.1697. Found: M^+, 342.1650).

Photochemistry of (bicyclo[4.1.0]hept-2-en-2-yloxy)trimethylsilane 11 with benzophenone. Formation of (9,9-diphenyl-8-oxatricyclo[5.2.0.0^{2,4}]nonan-1-yloxy)trimethylsilane 37, (8,8-diphenyl-9-oxatricyclo[5.2.0.0^{2,4}]nonan-1-yloxy)trimethylsilane 39, (8,8-diphenyl-1-trimethylsilyloxy-9-oxatricyclo[5.2.0.0^{2,4}]-nonan-6-yloxy)diphenylmethanol 38 and (2-trimethyl silyloxy-bicyclo[4.1.0]hept-3-en-2-yl)diphenylmethanol 40

A solution of **11** (1.05 g, 5.8 mmol) and benzophenone (1.26 g, 6.9 mmol) in acetonitrile (60 ml) were degassed and irradiated at 25 °C for 68 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the resulting residue was subjected to preparative thin layer chromatography using light petroleum (bp 60–80 °C)–ethyl acetate (9 : 0.5). A number of products were isolated and were identified to be oxetane **37** (R_f 0.55) (31 mg, 1.5%) obtained as a colourless oil, **39** (R_f 0.48) (42 mg, 2%), a white crystalline solid **38** (R_f 0.40) (18 mg, 0.6%), mp 126–128 °C and a white crystalline solid **40** (R_f 0.35) (136 mg, 6%), mp 62–64 °C.

For **37**: δ_H($CDCl_3$, 300 MHz) −0.05 (s, 9H), 0.35 (q, *J* 5.4, 1H), 0.46 (m, 1H), 0.82 (m, 1H), 1.03 (td, *J* 8.6, 5.4, 1H), 1.42 (m, 1H), 1.63 (m, 1H), 1.81 (dm, *J* 15.6, 1H), 2.07 (tt, *J* 13.6, 4.5, 1H), 4.52 (s, 1H), 7.13–7.70 (m, 10H); δ_C($CDCl_3$, 75 MHz) 1.9, 4.5, 13.6, 16.0, 18.1, 23.0, 82.1, 92.5, 125.1, 126.2, 126.4, 126.9, 127.3, 127.6, 143.3, 143.7, 1 × C not observed; ν_{max}/cm^{-1} 3056, 3020, 2926, 1447, 1357, 1250, 1159; *m*/*z* 364 ($M^{+\bullet}$, 4%), 183 (35), 182 (100), 167 (30), 149 (23), 105 (42), 77 (29), 75 (27), 73 (92), 69 (34), 57 (35), 55 (35); λ_{max}(CH_3CN)/nm 257, 220 (log ε 5.78, 6.98) (HRMS: $C_{23}H_{28}O_2Si$ requires $M^{+\bullet}$, 364.1855. Found: M^+, 364.1941).

For **39**: δ_H($CDCl_3$, 300 MHz) 0.13 (s, 9H), 0.46 (m, 2H), 0.72 (td, *J* 8.4, 5.1, 1H), 1.50 (m, 2H), 1.66 (m, 2H), 1.87 (m, 1H), 3.12 (br s, 1H), 7.12–7.54 (m, 10H); δ_C($CDCl_3$, 75 MHz) 1.7, 8.8, 14.3, 25.8, 27.2, 37.1, 44.0, 88.0, 108.2, 126.0, 126.1, 126.2, 126.4, 127.6, 127.9, 145.6, 147.7; ν_{max}/cm^{-1} 3063, 3020, 2956, 1446, 1311, 1249, 1150; *m*/*z* 364 ($M^{+\bullet}$, 0.93%), 182 (100), 167 (32), 73 (85); λ_{max}(CH_3CN)/nm 218 (sh), 204 nm (log ε 6.74, 6.87) (HRMS: $C_{23}H_{28}O_2Si$ requires $M^{+\bullet}$, 364.1858. Found: M^+, 364.1828).

For **38**: δ_H($CDCl_3$, 300 MHz) −0.05 (s, 9H), 0.62 (m, 2H), 0.95–1.30 (m, 4H), 1.65 (m, 1H), 2.95 (m, 1H), 3.68 (d, *J* 3.6, 1H), 6.73–7.71 (m, 20H); δ_C($CDCl_3$, 75 MHz) 1.6, 5.0, 13.4, 18.6, 23.6, 38.9, 53.0, 79.8, 83.2, 101.3, 124.6, 125.6, 126.0, 126.2, 126.8, 127.3, 127.4, 127.6, 128.0, 128.3, 128.6, 144.5, 145.6, 147.2, 148.9; ν_{max}/cm^{-1} 3412, 2359, 1641, 1446, 1250; *m*/*z* 528 ($M^{+\bullet}$ − H_2O, 0.54%), 183 (44), 182 (29), 181 (78), 167 (25), 105 (100), 77 (40), 75 (46), 73 (71); λ_{max}(CH_3CN)/nm 253.5, 219 (log ε 6.48, 7.34) (HRMS: $C_{36}H_{38}O_3Si$ requires $M^{+\bullet}$ − TMS − OH − Ph, 379.1698. Found: 379.1691).

For **40**: δ_H($CDCl_3$, 400 MHz) 0.09 (s, 9H), 0.45–2.20 (m, 7H), 5.50 (m, 1H), 5.58 (m, 1H), 7.10–7.80 (m, 10H); δ_C($CDCl_3$, 100 MHz) 2.3, 7.3, 11.9, 20.1, 24.3, 81.1, 83.7, 126.4, 126.9, 127.0, 128.7, 129.0, 144.6, 144.9, 2 × CH not observed; ν_{max}/cm^{-1} 3557, 3021, 2950, 1642, 1250, 1114; *m*/*z* 364 ($M^{+\bullet}$, 8%), 361 (28), 183 (22), 182 (28), 181 (100); λ_{max}(CH_3CN)/nm 258, 218 (sh) (log ε 5.87, 6.75) (Found: C, 75.5; H, 7.7. $C_{23}H_{28}O_2Si$ requires C, 75.8; H, 7.7%).

2-(1-Hydroxy-1,1-diphenylmethyl)bicyclo[4.1.0]hept-3-en-2-ol 44

To a solution of **40** (23 mg, 0.06 mmol) and 3 Å molecular sieves (10 mg) in dry dichloromethane (1 ml) at 0 °C was added tetrabutylammonium fluoride (72 μl, 1 M in THF). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting solution was diluted with water and extracted with dichloromethane. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified using HPLC [light petroleum (bp 40–60 °C)–diethyl ether elution, 6 : 1, 2.0 ml min^{-1}] to afford the title compound **44** as a white crystalline solid (t_R 30.0 min) (13 mg, 16%), mp 99–103 °C; δ_H($CDCl_3$, 300 MHz) 0.25–2.38 (m, 7H), 3.25 (br s, 1H), 5.52 (m, 1H), 5.63 (m, 1H), 7.20–7.75 (m, 10H); ν_{max}/cm^{-1} 3545, 3469, 3015, 2897, 1493, 1447, 1346; *m*/*z* 274 ($M^{+\bullet}$ − H_2O, 7%), 256 (22), 184 (22), 183 (84), 169 (58); λ_{max}(CH_3CN)/nm 257.5, 218 (sh) nm (log ε 5.88, 6.94) (HRMS: $C_{20}H_{20}O_2$ requires ($M^{+\bullet}$ − H_2O), 274.1358. Found: 274.1355).

4-Hydroxy-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid methyl ester 47

A solution of **12** (30 mg, 0.093 mmol) and benzophenone (19 mg, 0.10 mmol) in pentane (2.5 ml) were degassed and irradiated at 25 °C for 24 h using a medium pressure mercury lamp. The reaction mixture was concentrated under reduced pressure and the residue was purified using HPLC [9 : 1 light petroleum (bp 60–80 °C)–ethyl acetate elution, 2.0 ml min^{-1}] to afford an oil (t_R 9.3 min) (14.9 mg). To a solution of this oil (14.9 mg) and 3 Å molecular sieves (30 mg) in dry dichloromethane (0.5 ml) at 0 °C was added tetrabutylammonium fluoride (49 μl, 1 M in THF). The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting solution was diluted with water (1 ml) and extracted with dichloromethane (3 × 2 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified using preparative thin layer chromatography [light petroleum (bp 60–80 °C)–diethyl ether, 4 : 1] to afford a white crystalline solid **47** (R_f 0.17) (3 mg, 27%), mp 137–139 °C; δ_H($CDCl_3$, 400 MHz) 0.80–1.88 (m, 6H), 2.65 (t, *J* 6.2, 1H), 3.09 (t, *J* 6.2, 1H), 3.84 (s, 3H), 5.05 (s, 1H), 6.63 (d, *J* 8.8, 1H), 7.70 (d, *J* 8.8, 1H); δ_C($CDCl_3$, 100 MHz) 21.8, 22.6, 23.3, 28.4, 51.6, 111.4, 127.7, 127.8, 129.8, 141.9, 156.6, 167.9; ν_{max}/cm^{-1} 3324, 2920, 1724, 1581, 1431, 1260; *m*/*z* 206 ($M^{+\bullet}$, 53%), 180 (31), 175 (56), 174 (100), 173 (31), 149 (40), 148 (21), 147 (47), 146 (31), 145 (28), 131 (21), 121 (23), 115 (33), 107 (30), 105 (39), 91 (57), 79 (30), 77 (46), 71 (27), 69 (25), 65 (27), 57 (59), 55 (34), 51 (26); λ_{max}(CH_3CN)/nm 252, 219 (sh), 207 (log ε 6.26, 6.33, 6.40) (HRMS: $C_{12}H_{14}O_3$ requires $M^{+\bullet}$, 206.0943. Found: M^+, 206.0946).

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