Intramolecular Photocycloaddition of 3-Benzyloxyprop-1-enes

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The photochemistry of 3-benzyloxyprop-1-ene is markedly influenced by the presence of features which direct the intramolecular *meta* photocycloaddition to the 1,3-positions of the benzene ring and by constraining the benzylic position in the bichromophore. Thus, derivatives having 2′-methyl, 2′-methoxy and/or 1,1-dimethyl substitution yield *meta* photocycloadducts with the isomer having the linear triquinane unit greatly predominating. Adducts arising from 1,2-intramolecular attack are also observed from the substituted 3-benzyloxyprop-1-enes but the major by-product from 1-benzyloxy-3-methylbut-2-ene is the novel spiro compound **28** derived from an 'ene' type reaction. The indanyl vinyl ethers undergo *meta* photocycloaddition to give both the bridged linear and angular triquinane skeleta with the former again predominating, while for the corresponding unsubstituted tetralin derivative the angular isomer is formed in the greater yield and with the dimethyl compound **36**, the major photoisomer results from an initial intramolecular 1,2-attack in the bichromophore followed by thermal ring opening and 4π-photocyclisation.

The intramolecular *meta* photocycloaddition of ethenes to the benzene ring was first reported in 1971 for the (*Z*)- and (*E*)-6-phenylhex-2-enes by Morrison and co-workers.[1] Since this time, the features of benzene–ethene non-conjugated bichromophores which affect the efficiency and direct the regiochemistry of the photoaddition have been investigated by several groups.[2–8] In particular the influence of substituents on the arene, the propane chain connecting the chromophores, and the ethene have been largely elucidated.[3–7] Thus the directing influence of electron donor and acceptor substituents on the aryl moiety[3–5] are consistent with the pathway proposed for intermolecular systems[9] involving developing polarity in the S_1 benzene ring prior to bond formation with the ethene, and while substituents on the propane chain can adversely affect the desired conformation of the bichromophore thereby leading to inefficiency and low selectivity of the reaction,[3] interaction of a methyl substituent at the benzylic position with a 2′-substituent leads to stereoinduction in the cycloaddition.[8,10] Adverse effects may also arise from substitution on the ethene moiety but steric interactions in the (*Z*)- but not the (*E*)-isomer of 6-phenylhex-2-ene inhibit attack of the ethene at the 2′,6′-positions and the cycloaddition proceeds essentially specifically at the 1′,3′-positions of the benzene ring.[5,7]

The enormous potential of intramolecular *meta* photocycloaddition in complex molecule total synthesis has been extensively and elegantly demonstrated by Wender and co-workers over the past ten years.[8] The usefulness of the reaction as a key step towards [5.5.5.5]fenestranes has also been investigated by Keese and co-workers.[6,7] However, despite this intense interest in 5-phenylpent-1-ene derivatives, attempts to develop the photoreaction as a direct route to heterocyclic systems from benzene–ethene bichromophores linked by amino or ether units has seemingly attracted little attention.

Some time ago we noted[11] that *N*-methyl-*N*-phenalkyl allylamines **1** do not undergo intramolecular addition involving either the amino or vinyl moieties, although appreciable quenching of the benzene–amine intramolecular exciplex fluorescence[12] by the vinyl moiety was evident. Instead, the products from **1** were principally those of fragmentation. The position of an ether link in the three-unit chain joining the phenyl and vinyl groups has a marked influence on the photoreactions of the bichromophores.[2] Thus, while the major photoisomer **2** isolated from phenethyl vinyl ether reflects 2,5-addition of the ethene to the phenyl group, 4-phenoxybut-1-enes undergo extensive polymer formation on 254 nm irradiation and give only minor amounts of intramolecular *meta* cycloadducts.[3,13] The presence of an electron withdrawing group (COMe, CN or CO_2Me) in the 2′- or 4′-positions of the latter bichromophore, however induces an efficient intramolecular 1,2-cycloaddition which gives high yields of 4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-dienes as the photostable product.[14,15] In contrast, intramolecular *meta* photocycloaddition does occur with 3-benzyloxyprop-1-ene and the products reflect attack at both the 2′,6′- and 1′-,3′-positions of the benzene ring. It was suggested[2] that the lower reactivity of this bichromophore compared to that of 5-phenylpent-1-ene may arise from through-bond quenching of the S_1 state of the arene by the oxygen.

$Ph(CH_2)_mN(CH_3)(CH_2)_n\text{—}CH{=}CH_2$

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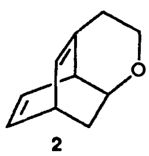

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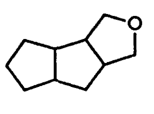
In this paper, we consider the influence of bichromophore structure on the photocycloaddition of 3-benzyloxyprop-1-enes and although these intramolecular cycloadditions may be less efficient than those of 5-phenylpent-1-enes, chemical yields and conversions can be very good, few by-products are generally formed, and, most importantly, greater reaction selectivity is evident particularly in the direction of cyclopropane ring formation in the *meta* cycloadducts than is observed for the corresponding hydrocarbon systems.

Results and Discussion

In principle, the intramolecular *meta* photocycloaddition of 3-benzyloxyprop-1-enes offers a direct route to linear and angular oxatriquinane systems **3** and **4** respectively. The parent bichromophore **5**, however, undergoes the intramolecular *meta* addition with low regioselectivity of attack of the ethene onto the benzene ring and the same lack of selectivity in the direction of formation of the cyclopropane in the adducts is apparent as is observed for 5-phenylpent-1-ene and most of its derivatives.[3–10] These earlier findings were verified in the present work with the exception that the 1:1:1.5 ratio quoted[2] for the 1,6-, 5,6- and



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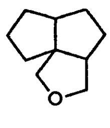

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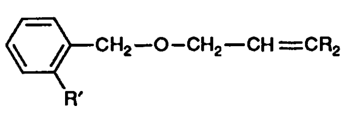
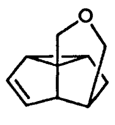


5 R = R′ = H
6 R = H, R′ = Me
7 R = H, R′ = OMe
8 R = Me, R′ = H
9 R = R′ = Me
10 R = Me, R′ = OMe



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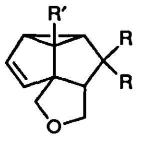
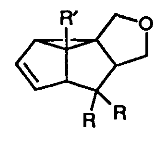


12 R = R′ = H
13 R = H, R′ = Me
14 R = H, R′ = OMe



15 R = R′ = H
16 R = H, R′ = Me
17 R = H, R′ = OMe
18 R = Me, R′ = H
19 R = R′ = Me
20 R = Me, R′ = OMe

Table 1 Intramolecular photoreactions of 3-benzyloxyprop-1-enes

Bichromophore	Photoisomers	Initial ratio^{a}	Final ratio^{b}	Yield (%)^{c}
5	**11**:**12**:**15**	1:2:2	1:1:2	59
6	**16**:**23** **22**^{d}	4:1	12:1	60
7	**17**:**24**	2.25:1	2.5:1	68

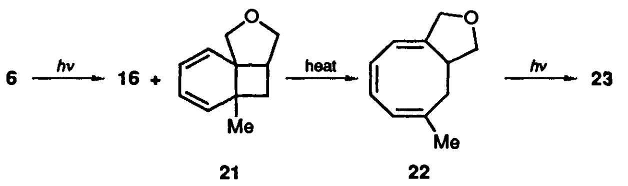
^{a} At shortest exposure time (generally 1 h) for accurate integration of products. ^{b} At exposure time when product ratio does not change. ^{c} No attempts were made to optimise yields of photoisomers but values quoted are corrected for amounts of the bichromophore unconverted. ^{d} Only observed from preparative scale experiments.

7,8-bridged dihydrosemibullvalenes **11**, **12** and **15** respectively was not assessed at very short exposure time in the earlier study. It is now well-known that ratios of intramolecular adducts from arene–ethene bichromophores are time variant.[4,5] This feature arises from the differing efficiencies of the photoinduced vinylcyclopropane–cyclopentene isomerisation which interconverts *meta* cycloadduct isomers, and at the earliest time of their reliable estimation, the intramolecular adduct ratio from **5** was 1:2:2 respectively.

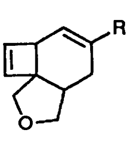
The present study initially involved an assessment of the effectiveness, on the intramolecular photocycloaddition of 3-benzyloxyprop-1-enes, of the structural features which are known to direct the regiochemistry of the intramolecular addition of 5-phenylpent-1-ene derivatives.[2–5] 2′-Methyl- and 2′-methoxy-substituents orient the attack of the intramolecular photocycloaddition of the ethene of 5-phenylpent-1-enes specifically to the 1,3-positions of the benzene ring as a consequence of their ability to stabilise the developing positive charge of the polarity which arises in the S$_1$ arene ring on approach of the ethene.[4,5] The results from 254 nm irradiation of 1% w/v of the 2′-methyl- and 2′-methoxy-substituted 3-benzyloxyprop-1-enes in cyclohexane solution are given in Table 1 along with those of the parent bichromophore. There are several aspects of these results which require comment.

As expected from the photochemistry of 5-phenylpent-1-enes, the 2′-methyl and 2′-methoxy substituents direct the intramolecular photocycloaddition in the ether-linked bichromophores to the 1,3-positions of the arene. However, the apparent specificity of both the 2′-methyl and 2′-methoxy bichromophores **6** and **7** in undergoing the cyclopropane ring formation to give the linear oxatriquinane was not expected from the previous studies of the parent 3-benzyloxyprop-1-ene or the hydrocarbon bichromophores. Indeed both the 2′-methyl and 2′-methoxy derivatives of 5-phenylpent-1-ene result in initial ratios of the linear and angular systems of approximately 1:1.2 respectively.[3] A somewhat similar lack of selectivity is reported from irradiation of the 2′-methoxy derivatives of the (*Z*)- and (*E*)-6-phenylhex-2-enes, and the 2′-methyl substituted (*Z*)-isomer.[4,5] Ratio changes favouring the linear triquinane isomer with increased exposure times have been previously reported,[4] and it may be argued that the presently observed 'specificity' arises from a very facile photoinduced conversion of the angular into the linear isomer. The preference for the linear triquinane from prolonged 254 nm irradiation of the 2′- and 4′-cyano substituted derivatives of (*E*)-6-phenylhex-2-ene can be readily understood in terms of the greater absorptivity (estimated to be *ca.* 10–15 fold in the 260 nm region) of the 4- than the 2-cyano dihydrosemibullvalene moiety of the intramolecular *meta* cycloadducts.[5] However, in the present systems, the vinylcyclopropane chromophores in the linear intramolecular cycloadducts **16** and **17** would be closely similar to those of the corresponding angular isomers **13** and **14** respectively and would not be expected to have significantly different absorptivities which could be held responsible for preferential photoisomerisation and the observation of solely the linear triquinane isomer. The overwhelming predominance of the linear triquinane photoisomers at even very short exposure times from both **6** and **7** must arise from another structural feature.

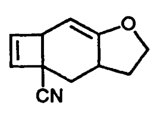
The formation of the photoisomers **23** and **24** from the bichromophores **6** and **7** respectively is considered to arise by the sequence, outlined in Scheme 1 involving 1,2-photocycloaddition, disrotatory ring opening of the thermally labile primary *ortho* cycloadduct **21** to give the cyclo-octa-1,3,5-triene isomer (*e.g.* **22**) which then undergoes intramolecular disrotatory photocyclisation. This type of intramolecular photocycloaddition has only been previously reported for 4-phenoxybut-1-enes having a strongly electron withdrawing group (*e.g.* –CN, –COMe) in the 2′- or 4′-positions,[14,15] or for 1-(but-3-enyl)-7-methoxyindanes.[6,7] Furthermore, the intermediate cyclo-octa-1,3,5-triene from these bichromophores undergoes the subsequent disrotatory photocyclisation to give solely the 'linear' structural isomer (*e.g.* **25**). This feature may be



Scheme 1



23 R = Me
24 R = OMe



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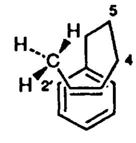

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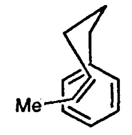

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Table 2 Intramolecular photoreactions of 1-benzyloxy-3-methylbut-2-enes

Bichromophore	Photoisomers	Initial ratio[a]	Final ratio[b]	Yield (%)[c]
8	**18**:**28**[d]	1.3:1	1.4:1	60
9	**19**:**29**[e]	2:1	100% (**27**)	81
10	**20**:**30**	1.7:1	6.25:1	95

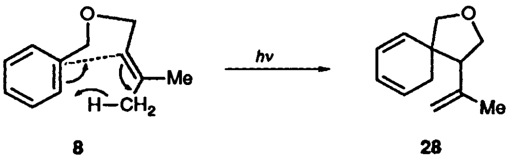
[a–c] As in Table 1. [d] At very low conversions of the bichromophore other photoisomers were detected but these rapidly disappeared on continued irradiation and were not present in isolable amounts from preparative experiments. [e] Tentative structural assignment made on the basis of characteristic ^1H NMR signals[15] in the product mixture at low conversions of the bichromophore.

accounted for in terms of preferential excitation of the more strongly absorbing diene unit of the cyclo-octa-1,3,5-triene from the substituted 4-phenoxybut-1-enes, and formation of the less strained product from the cyclo-octatriene from the indan derivative. In contrast, photoisomerisation of the cyclo-octa-1,3,5-trienes from **6** and **7** give solely the 'angular' structure by cyclisation of the 1,3-rather than the 3,5-diene unit possibly because the former is more planar than the latter as a result of the constraining tetrahydrofuran moiety.

The above results show that the ethereal oxygen in the 4-position of 5-phenylpent-1-enes has a dramatic effect on the photochemistry of the bichromophore when there is a directing substituent (*i.e.* –Me, or –OMe) present on the arene. In these cases, the direction of cyclopropane ring formation is essentially specific in the *meta* photocycloaddition intermediate. Furthermore, *ortho* photocycloaddition, albeit as a minor process, is observed.

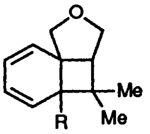
A further feature which may be used to direct the intramolecular *meta* photocycloaddition of 5-phenylpent-1-enes to the arene 1′,3′-positions is the presence of a (*Z*)-1-methyl group. This directing influence originates from the considerable steric hindrance between the hydrogens on C-2′, C-4 and C-5 with those of the methyl group in the conformation **26** required for 2′,6′-attack. Such problems are not evident in the conformation **27** which precedes cycloaddition at the arene 1′, 3′-positions.[5] The photocycloaddition reactions of (*Z*)- and (*E*)- arene–ethene bichromophores can be complicated by photoinduced interconversion between the isomers. Accordingly, we have investigated the intramolecular photocycloaddition reactions of 1-benzyloxy-3-methylbut-2-ene **8** and the 2′-methyl and 2′-methoxy derivatives **9** and **10** respectively: these data are summarised in Table 2. It is evident from these results that there remains sufficient steric interaction in the absence of a methylene unit at the 5-position (see **26**) to ensure that the conformation for 2′,6′-addition is unfavoured and specific 1′,3′-attack thus occurs. Again the cyclopropane ring formation is apparently specific and only the linear triquinane isomers of the intramolecular *meta* photocycloadducts are isolated even from **8** which has no directing substitutent on the phenyl ring. The minor products from irradiation of the bichromophores **9** and **10** can again be accounted for by an initial intramolecular 1,2-photocycloaddition to the benzene ring. However, the formation of the spiro compound **28** from **8** is, to our knowledge, unprecedented in phenyl–vinyl bichromophore photochemistry although the formation of an isomer which 'is not a *meta* adduct' from (*E*)-1-benzyloxybut-2-ene has been noted by Neijenesch.[13] The suggested route to **28** is outlined in Scheme 2 and is an intramolecular example of the 'ene'-type addition reported from the reaction of 2,3-dimethylbut-2-ene with S_1 benzene.[16]

Both Keese and co-workers[6,7] and ourselves[17] have investigated the reactivity of arene–vinyl bichromophores in which the benzylic position is constrained. In particular, we have observed that 4-(indan-1′-yl)but-1-ene undergoes efficient intramolecular photocycloaddition to the 1,3-positions of the arene to give the bridged linear and angular triquinanes **31** and **39** respectively in an approximate ratio of 1:1. The greater flexibility of the tetrahydronaphthalene derivative **34** allows addition at both the 2,6- and 1,3-arene positions and from the latter positions of attack, the bridged linear isomer predominates. In order to assess if the remarkable selectivity effects described above for arene–ethene bichromophores having a $-CH_2OCH_2-$linking unit are applicable to the more constrained molecules, we investigated the 254 nm induced reactions of the indane and tetrahydronaphthalene derivatives **37**, **38**, **35** and **36**. These results are presented in Table 3.

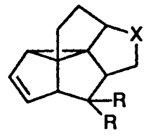


8 **28**

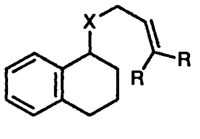
Scheme 2



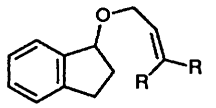
29 R = Me
30 R = OMe



31 X = CH₂, R = H
32 X = O, R = H
33 X = O, R = Me

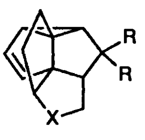


34 X = CH₂, R = H
35 X = O, R = H
36 X = O, R = Me

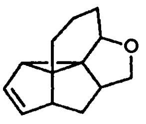


37 R = H
38 R = Me

The intramolecular photoaddition of the indanyl compound **37**, yet again, illustrates the considerable influence of the ether linking unit and provides a very rare example in arene–ethene bichromophoric systems of a specific mode of photoaddition accompanied by extremely selective, if not specific, direction in cyclopropane ring formation in the *meta* cycloaddition. Indeed, the bridged angular isomer **40** was not detected from small-scale experiments but was detected in small amounts from preparative irradiations at low conversions of the bichromophore **37**. Unfortunately, the specificity is lost on 1,1-dimethyl



39 X = CH₂, R = H
40 X = O, R = H
41 X = O, R = Me



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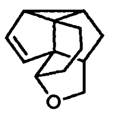

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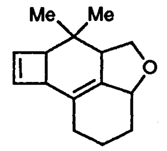

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Table 3 Intramolecular photoreactions of 3-indan-1′-yloxyprop-1-enes and 3-(1′,2′,3′,4′-tetrahydro-1′-naphthyloxy)prop-1-enes

Bichromophore	Photoisomers	Initial ratio[a]	Final ratio[b]	Yield (%)[c]
37	**32**, **40**	See text	See text	70
38	**33**:**41**	2.3:1	5:1	98
35	**42**:**43**	1:1.1	1:1.7	47
36	**44**:X[d]	2:1	4:1	17

[a–c] As in Table 1. [d] Minor isomer not isolated.

substitution of the prop-1-enyl chain and the reaction of **38** is merely selective but again the reaction markedly favours the formation of the linear triquinane isomer. Furthermore, the change in the ratio with time illustrates the considerably greater photolability of the angular compared to the linear isomer even in systems which are expected to have closely similar absorption properties of the ethenyl cyclopropane chromophores. Relaxing the degree of constraint as in the tetrahydronaphthalene derivative **35**, has a surprising effect for not only is the angular triquinane isomer now favoured, albeit marginally, but also the final ratio of products shows that, in contrast to the intramolecular cycloadducts from **38**, the bridged angular isomer **43** is more photostable than the bridged linear isomer **42**. Again dimethyl substitution of the ethene markedly affects the photoreaction and in this case promotes the 1,2-cycloaddition process to give the isomer **44** which is analogous to the major products reported from 4-(7′-methoxyindan-1′-yl)but-1-enes.[7]

With the exception of the tetrahydronaphthalene bichromophores, the present results and their comparison with those published for 5-phenylpent-1-enes, clearly illustrate that in intramolecular photocycloaddition reactions of arene–ethene bichromophores, the selectivity in formation of the linear and angular triquinane isomers can be markedly influenced by the linking unit. The origin of this directing effect of the ether link may lie in the somewhat smaller angle of the $-CH_2OCH_2-$ than the $-CH_2CH_2CH_2-$ unit. Molecular models indicate that this feature gives a conformation of the ether-linked bichromophore which allows a closer and more directly opposite approach of the C-2 of the ethene and C-1′ of the arene than is the case with the propane link. Assuming that this feature promotes more rapid bonding between C-2 and C-1′ than between the other two centres (*i.e.* C-1 and C-3′), then the prior development of a tetrahedral carbon at C-1′ may well be sufficient to favour cyclopropane ring formation between C-2′ and C-6′ compared to C-2′ and C-4′. A similar argument involving difference in the rate of formation of the bonds between the arene and the ethene has been put forward by Professor Cornelisse to explain the appreciably lower selectivity in cyclopropane ring formation in the intermolecular photocycloaddition of a variety of 1,2-disubstituted benzenoid compounds to cyclopentene.[18] At present, it is not, however, obvious why this effect in the ether-linked bichromophore only operates in the presence of features which direct the photocycloaddition to the 1,3-positions of the arene and is seemingly not evident in the parent compound **5**.

Experimental

Photochemical and Analytical Methods.—Preparative irradiations were of 1% w/v solutions (150 cm^3) of the bichromophores in cyclohexane and used two low pressure mercury arc lamps each rated at 30 W. Periodic cleaning of the irradiation tubes appreciably improved rates of bichromophore conversions. The irradiations were monitored by GC using a Hewlett-Packard 5790A instrument fitted with a flame ionisation detector and a 12 m BP1 (SGE OV1 equivalent) bonded phase capillary column. 2,2,4,4,6,8,8-Heptamethylnonane was used as the GC standard in experiments to assess percentage conversions of the starting materials and yields of adduct isomers. Analysis of product mixtures by TLC used Camlab Polygram G/UV precoated sheets and varying proportions of 40–60 b.p. light petroleum and diethyl ether as the eluent. Separation and purification of the photoisomers were achieved either by flash chromatography on ICN silica 32–63 (Park Scientific Ltd) or by preparative GC using a Perkin-Elmer F21 instrument fitted with 64 mm i.d. × 1 m columns packed with 15% w/w OV101 on 80–100 Chromosorb P. NMR spectra were recorded on a JEOL FX90Q, a Bruker WM250 or a Bruker WH400 (SERC Spectrometer Service, Warwick) instrument with tetramethylsilane as an internal standard and in $CDCl_3$ solution unless otherwise stated: all coupling constants are given in Hz. IR spectra were obtained using a Perkin-Elmer 881 spectrophotometer and were of liquid films. Accurate mass data were provided by the SERC Mass Spectrometry Service Centre, Swansea, after chromatographic purity assurance.

Bichromophores.—The aryl–vinyl bichromophores were synthesised by the common method of reaction of allyl bromide or 4-bromo-2-methylbut-2-ene with the appropriate arylmethyl alcohol under basic conditions. The synthesis of 1-benzyloxy-3-methylbut-2-ene **8** is given to illustrate the procedure. Sodium hydride (3 g, 60% dispersion) was washed with 30–40 °C b.p. light petroleum (3 × 50 cm^3) under nitrogen. The light petroleum was removed and benzyl alcohol (6.1 g, 0.0568 mol) in dry dimethyl formamide (30 cm^3) was added slowly with stirring over 30 min. When effervescence had ceased, 4-bromo-2-methylbut-2-ene was added to the vigorously stirred mixture over 20 min. The reaction mixture was then heated at 50 °C for 4 h, by which time complete consumption of the benzyl alcohol was evident by TLC. Hydrochloric acid (2 mol dm^{-3}; 150 cm^3) was added to the cooled mixture and the product was extracted with diethyl ether (3 × 50 cm^3) and the combined extracts were dried over anhydrous magnesium sulfate. Removal of the ether by distillation and vacuum distillation of the resulting yellow residue (0.05 mmHg, 130–140 °C) gave **8** as a colourless liquid, pure by GC and TLC, in 65% yield.

3-Benzyloxyprop-1-ene **5** has been previously described.[2]

3-(2′-*Methylbenzyloxy*)*prop*-1-*ene* **6**. δ_H 7.35–7.09 (overlapping ms, 3′-, 4′-, 5′-, 6′-H), 5.95 (ddt, $J_{2a,3a}$ 15.9, $J_{2,3b}$ 11.6, $J_{2,1}$ 6.0, 2-H), 5.29 (dq, $J_{3a,3b}$ 1.6, $J_{3a,1}$ 1.6, 3-H$_a$), 5.18 (dq, $J_{3b,1}$ 1.6, 3-H$_b$), 4.48 (s, $-CH_2O-$), 4.01 (dt, allylic $-CH_2-$), and 2.31 (s, $-CH_3$); δ_C(22.5 MHz), 136.56, 136.15, 134.82, 130.15, 128.50, 127.70, 125.70, 116.91, 71.19, 70.46 and 18.73; ν_{max}/cm^{-1} 1685 m and 1084 s (Found: M$^+$, 162.1044. Calc. for $C_{11}H_{14}O$: *M*, 162.1045).

3-(2′-*Methoxybenzyloxy*)*prop*-1-*ene* **7**. δ_H 7.48–6.85 (overlapping ms, 3′-, 4′-, 5′-, 6′-H), 5.98 (ddt, $J_{2,3a}$ 16.7, $J_{2,3b}$ 10.7, $J_{2,1}$ 5.9, 2-H), 5.37 (dq, $J_{3a,3b}$ 1.3, $J_{3a,1}$ 1.3, 3-H$_a$), 5.25 (dq, $J_{3b,1}$ 1.3, 3-H$_b$), 4.60 (s, $-CH_2O-$), 4.12 (dt, allylic $-CH_2-$) and 3.85 (s, Me); ν_{max}/cm^{-1} 1676m and 1086s (Found: M$^+$, 178.0994. Calc. for $C_{11}H_{14}O_2$: *M*, 178.0994).

1-*Benzyloxy*-3-*methylbut*-2-*ene* **8**. δ_H 7.38–7.20 (overlapping ms, 2′-, 3′-, 4′-, 5′-, 6′-H), 5.40 (t with fine coupling, $J_{2,1}$ 6.9), 4.49 (s, $-CH_2O-$), 3.98 (d, allylic $-CH_2-$), 1.76 (s, Me) and 1.65 (s, Me); δ_C(22.5 MHz), 138.56, 137.00, 128.24, 127.71, 127.41, 121.10, 71.99, 66.55, 25.73 and 17.98; ν_{max}/cm^{-1} 1679m and 1072s (Found: M$^+$, 176.1202. Calc. for $C_{12}H_{16}O$: *M*, 176.1201).

1-(2′-Methylbenzyloxy)-3-methylbut-2-ene **9**. δ_H 7.35–7.08 (overlapping ms, 3′-, 4′-, 5′-, 6′-H), 5.40 (t with fine coupling, $J_{2,1}$ 6.7), 4.48 (s, $-CH_2O-$), 4.00 (d, allylic $-CH_2-$), 2.32 (s, aryl Me), 1.78 (s, Me) and 1.67 (s, Me); ν_{max}/cm^{-1} 1676m and 1074s (Found: M$^+$, 190.1358. Calc. for $C_{13}H_{18}O$: *M*, 190.1353).

1-(2′-*Methoxybenzyloxy*)-3-*methylbut*-2-*ene* **10**. δ_H 7.40–6.78 (overlapping ms, 3′-, 4′-, 5′-, 6′-H), 5.42 (t with fine coupling,

$J_{2,1}$ 6.8), 4.56 (s, –CH_2O–), 4.04 (d, allylic –CH_2–), 3.79 (s, OMe), 1.76 (s, Me) and 1.67 (s, Me); δ_C 157.10, 136.62, 128.43, 127.92, 126.92, 121.39, 120.33, 110.13, 66.84, 55.25, 29.67, 25.73 and 17.97; ν_{max}/cm^{-1} 1676m and 1081s (Found: M$^+$, 206.1306. Calc. for $C_{13}H_{18}O_2$: *M*, 206.1302).

3-(Indan-1'-yloxy)prop-1-ene **37**. δ_H 7.41–7.15 (overlapping ms, 5'-, 6'-, 7'-, 8'-H), 5.96 (ddt, $J_{2,3a}$ 17.2, $J_{2,3b}$ 10.3, $J_{2,1}$ 5.55, 2-H), 5.31 (dq, $J_{3a.3b}$ 1.63, $J_{3a,1}$ 1.63, 3-H$_a$), 5.17 (dq, $J_{3b,1}$ 1.63 3-H$_b$), 4.96 (dd, $J_{1',2'a}$ 4.34, $J_{1',2'b}$ 6.57, 1'-H), 4.08 (ddt, allylic –CH_2–), 3.07 (ddd, $J_{3'a,3'b}$ 15.9, $J_{3'a,2'a}$ 8.35, $J_{3'a,2'b}$ 5.93, 3'-H$_a$), 2.78 (ddd, $J_{3'b,2'b}$ 8.29, $J_{3'b,2'a}$ 5.45, 3'-H$_b$), 2.33 (dddd, 2'-H$_b$) and 2.08 (dddd, 2'-H$_a$); δ_C 143.90, 142.76, 135.24, 128.24, 126.21, 124.97, 124.80, 116.63, 82.63, 69.52, 32.47 and 30.14; ν_{max}/cm^{-1} 1646m and 1075s (Found: M$^+$, 174.1045. Calc. for $C_{12}H_{14}O$: *M*, 174.1045).

1-(*Indan*-1'-*yloxy*)-3-*methylbut*-2-*ene* **38**. δ_H 7.42– 7.14 (overlapping ms 5'-, 6'-, 7'-, 8'-H), 5.40 (septet of t, $J_{2,1}$ 6.86, $J_{2,Me}$ 1.38, 2-H), 4.94 (dd, $J_{1',2'a}$ 4.26, $J_{1',2'b}$ 6.60, 1'-H), 4.08 (d, 1-H$_a$, 1-H$_b$), 3.09 (ddd, $J_{3'a,3'b}$ 15.9, $J_{3'a.2'a}$ 8.39, $J_{3'a,2'b}$ 6.00, 3'-H$_a$), 2.79 (ddd, $J_{3'b,2'b}$ 8.36, $J_{3'b,2'a}$ 5.45, 3'-H$_b$), 2.34 (dddd, 2'-H$_b$), 2.09 (dddd, 2'-H$_a$), 1.75 (s, Me) and 1.67 (s, Me); δ_C 143.90, 143.00, 136.54, 128.15, 126.18, 125.04, 124.77, 121.56, 82.46, 65.07, 32.48, 30.20, 25.77 and 18.06; ν_{max}/cm^{-1} 1685m and 1076s (Found: M$^+$, 202.1357. Calc. for $C_{14}H_{18}O$: *M*, 202.1356).

3-(1',2',3',4'-*Tetrahydro*-1'-*naphthyloxy*)*prop*-1-*ene* **35**. δ_H 7.60–7.20 (overlapping ms 6'-, 7'-, 8'-, 9'-H), 6.16 (ddt, $J_{2,3a}$ 17.6, $J_{2,3b}$ 10.1, $J_{2,1}$ 5.30, 2-H), 5.50 (dq, $J_{3a,3b}$ 1.50, $J_{3a,1}$ 1.50, 3-H$_a$), 5.36 (dq, $J_{3b,1}$ 1.50 3-H$_b$), 4.64 (t, $J_{1',2'}$ 4.4, 1'-H), 4.25 (t, allylic –CH_2–), 3.08–2.78 (m, 2'-H$_a$, 2'-H$_b$) and 2.24–1.80 (ms, 3'-H$_a$, 3'-H$_b$, 4'-H$_a$, 4'-H$_b$); ν_{max}/cm^{-1} 1686m and 1061s (Found: M$^+$, 188.1201. Calc. for $C_{13}H_{16}O$: *M*, 188.1197).

1-(1',2',3',4'-*Tetrahydro*-1'-*naphthyloxy*)-3-*methylbut*-2-*ene* **36**. δ_H 7.45–7.03 (overlapping ms 6'-, 7'-, 8'-, 9'-H), 5.42 (septet of t, $J_{2.1}$ 6.89, $J_{2,Me}$ 1.23, 2-H), 4.44 (t, $J_{1',2'}$ 4.60, 1'-H), 4.09 (t, 1-H$_a$, 1-H$_b$), 2.95–2.62 and 2.08–1.87 (overlapping ms, 2'-H$_a$, 2'-H$_b$, 3'-H$_a$, 3'-H$_b$, 4'-H$_a$, 4'-H$_b$), 1.74 (s, Me) and 1.68 (s, Me); δ_C 137.50, 137.08, 136.44, 129.27, 128.80, 127.53, 126.15, 121.80, 74.45, 64.84, 29.25, 28.06 and 18.82; ν_{max}/cm^{-1} 1674m and 1074s (Found: M$^+$, 216.1515. Calc. for $C_{15}H_{20}O$: *M*, 216.1514).

Photoproducts.—The spectral data for the intramolecular *meta* photocycloadducts **11**, **12** and **15** from 254 nm irradiation of 1-benzyloxyprop-2-ene have been previously reported.[2]

2-*Methyl*-10-*oxatetracyclo*[6.3.0.0^{1,3}.0^{2,6}]*undec*-4-*ene* **16**. δ_H(CDCl$_3$) 5.66 (dd, $J_{4,5}$ 5.6, $J_{4,3}$ 2.2, $J_{4,6}$ 0.4, 4-H), 5.44 (dd, $J_{5,6}$ 2.4, $J_{5.3}$ 0.7, 5-H), 3.90–3.60 (m, $J_{11,11'gem}$ 8.0, $J_{9,9'gem}$ 8.0, 11-, 11'-, 9-, 9'-H), 2.98 (dd, $J_{6,7}$ 3.4, 6-H), 2.38 (qd, $J_{8,7endo}$ 7.0, $J_{8.7exo}$ 7.0, $J_{8,9endo}$ 7.0, $J_{8,9exo}$ 3.0, 8-H), 1.83–1.80 (m, $J_{7,7'gem}$ 8.4, 7-, 7'-H), 1.71 (d, 3-H) and 1.29 (s, Me); δ_C 133.01, 128.88, 73.48, 67.29, 57.79, 50.99, 45.29, 42.79, 38.08 and 13.68 (Found: M$^+$, 162.1044. Calc. for $C_{11}H_{14}O$: *M*, 162.1045).

3-*Methyl*-10-*oxatricyclo*[6.3.0.0^{5,8}]*undeca*-3,6-*diene* **23**. δ_H 6.08 (d, $J_{6,7}$ 2.7, 7-H), 5.78 (d, 6-H), 5.65 (dq, $J_{4,5}$ 6.1, $J_{4,Me}$ 2.7, 4-H), 4.48 (d with fine couplings, $J_{11,11'}$ 12.9, 11-H), 4.27 (d with fine couplings 11'-H), 4.18 (t, $J_{9,9'}$ 8.1, $J_{9,5}$ 8.1, 9-H), 3.37 (t, $J_{9',5}$ 8.1, 9'-H), 2.90 (d, $J_{5,4}$ 6.1, 5-H), 1.87 (dd, $J_{1,2}$ 5.2, $J_{1,2'}$ 12.7, 1-H), 1.23 (br s, –CH_3) and 0.92–0.85 (m, 2-H, 2'-H); δ_C 143.20, 141.35, 133.56, 124.97, 73.81, 70.26, 48.78, 37.28, 36.48 and 25.76; *m*/*z* 162 (M$^+$).

6-*Methyl*-10-*oxabicyclo*[6.3.0]*undeca*-1,3,5-*triene* **22**. δ_H 5.32 (m, 5-H), 5.22 (t, $J_{3,2}$ 6.7, $J_{3,4}$ 6.7, 3-H), 4.79 (dd, $J_{2,3}$ 6.7, $J_{2,4}$ 1.9, 2-H), 3.97 (dd, $J_{9,9}$ 8.6, $J_{9,8}$ 7.6, 9-H), 3.78 (d, $J_{11,11'}$ 8.9, 11-H), 3.64 (d, 11'-H), 3.53 (dd, $J_{9',1}$ 4.6, 9'-H), 2.07 (dq, $J_{7,7'}$ 15.0, 7-H), 1.71 (dq, 7'-H), 1.24 (s, Me) and 1.04 (d, 8-H).

2-*Methoxy*-10-*oxatetracyclo*[6.3.0.0^{1,3}.0^{2,6}]*undec*-4-*ene* **17**. δ_H(CDCl$_3$) 5.70 (dd, $J_{4,5}$ 5.7, $J_{4,3}$ 2.4, 4-H), 5.57 (ddd, $J_{5,6}$ 2.7, $J_{5,3}$ 1.3, 5-H, 3.91 (dd, $J_{9,9'gem}$ 8.9, 9-H), 3.87 (dd, $J_{11,11'gem}$ 8.9, 11-H), 3.70 (dd, 9'-H), 3.69 (d, 11'-H), 3.43 (s, –OCH_3), 3.42 (ddd, $J_{6,7exo}$ 4.2, $J_{6,7endo}$ 1.8, 8-H), 2.28 (qd, $J_{8.7endo}$ 8.0, $J_{8.7exo}$ 8.0, $J_{8,9endo}$ 8.0, $J_{8,9exo}$ 3.1, 8-H), 2.22 (dd, 3-H) and 1.98–1.91 (m, $J_{7,7'}$ 8.9, 7-H, 7'-H); *m*/*z* 178 (M$^+$).

3-*Methoxy*-10-*oxatricyclo*[6.3.0.0^{5,8}]*undeca*-3,6-*diene* **24**. δ_H 6.17 (d, $J_{6,7}$ 2.8, 7-H), 6.07 (d, 6-H), 5.62 (dq, $J_{4,5}$ 6.0, $J_{4,OMe}$ 2.9, 4-H), 4.41 (d with fine couplings $J_{11,11'}$ 12.0, 11-H), 4.28 (d with fine couplings $J_{11,11'}$ 12.0, 11-H), 4.28 (d with fine couplings, 11'-H), 4.22 (t, $J_{9,9'}$ 8.0, $J_{9,5}$ 8.0, 9-H), 3.45–3.32 (m, 9'-H, 5-H), 3.33 (br s, –OCH_3), 2.12 (dd, $J_{1,2'}$ 12.3, $J_{1,2}$ 5.2, 1-H) and 1.32–1.20 (m, 2-H, 2'-H); δ_C 145.64, 138.55, 137.05, 115.20, 85.23, 73.91, 70.19, 52.00, 46.71, 37.06 and 33.28; *m*/*z* (M$^+$) 178.

7,7-*Dimethyl*-10-*oxatetracyclo*[6.3.0.0^{1,3}.0^{2,6}]*undec*-4-*ene* **18**. δ_H(CDCl$_3$) 5.77 (dd, $J_{4,5}$ 5.5, $J_{4,3}$ 2.3, $J_{4,6}$ 0.4, 4-H), 5.53 (dd, $J_{5,6}$ 2.6, 5-H), 3.90 (dd, $J_{9,9'}$ 7.4, $J_{9,8}$ 1.9, 9-H), 3.67 (d, $J_{11,11'}$ 8.9, 11-H), 3.64 (dd, $J_{9',8}$ 9.6, 9'-H), 3.58 (d, 11'-H), 2.75 (dd, $J_{2,6}$ 5.4, 6-H), 2.41 (t, $J_{2,3}$ 5.4, 2-H), 2.00 (dd, 3-, 8-H), 1.11 (s, Me) and 0.82 (s, Me); δ_C 132.19, 129.90, 70.70, 68.03, 63.50, 57.25, 50.11, 47.33, 42.08, 32.05, 23.56 and 23.51 (Found: M$^+$, 176.1196. Calc. for $C_{12}H_{16}O$: *M*, 176.1201).

4'-(*Allyl*)*spiro*(*cyclohexa*-2,4-*diene*-1,3'-*tetrahydrofuran*) **28**. δ_H 5.80–5.76 (overlapping ms, 2-H, 5-H), 5.64 (ddd, $J_{3,2}$ 10.4, $J_{3,4}$ 4.1, $J_{3,5}$ 2.0, 3-H), 5.58 (ddd, $J_{4,5}$ 10.1, $J_{4,2}$ 2.1, 4-H), 4.82 (br s, 1''$_a$-H), 4.65 (br s, 1''$_b$-H), 4.08 (t, $J_{5'a,5'b}$ 8.6, $J_{5'a,4'}$ 8.6, 5'$_a$-H), 3.99 (t, $J_{5'b,4'}$ 8.6, 5'$_b$-H), 3.68 (d, $J_{2'a,2'b}$ 8.6, 2'$_a$-H), 3.68 (d, 2'$_b$-H), 2.65–2.61 (overlapping ms, 6$_a$-H, 6$_b$-H, 4'-H) and 1.69 (s, –CH_3); δ_C (100.6 MHz; CDCl$_3$) 142.46 (C-2''), 130.87 (C-2), 127.55 (C-5), 124.96 (C-3), 124.04 (C-4), 111.26 (C-3''), 80.79 (C-2'), 70.62 (C-5'), 56.55 (C-4'), 46.70 (C-1,3'), 26.29 (C-6) and 23.46 (C-3'') (Found: M$^+$, 176.1196. Calc. for $C_{12}H_{16}O$: *M*, 176.1201).

2,7,7-*Trimethyl*-10-*oxatetracyclo*[6.3.0.0^{1,3}.0^{2,6}]*undec*-4-*ene* **19**. δ_H(CDCl$_3$) 5.76 (dd, $J_{4,5}$ 5.5, $J_{4,3}$ 2.2, $J_{4,6}$ 0.4, 4-H), 5.55 (dd, $J_{5,6}$ 2.5, $J_{5,3}$ 0.7, 5-H), 3.86 (dd, $J_{9,9'}$ 9.4, $J_{9,8}$ 1.9, 9-H), 3.67–3.57 (ms, $J_{11,11'}$ 8.9, 11-H, 11'-H, 9-H), 2.50 (d, 6-H), 2.05 (dd, $J_{8,9}$ 7.7, $J_{8,9'}$ 1.9, 8-H), 1.56 (d, 3-H), 1.30 (s, Me on C-1), 1.06 (s, Me on C-7) and 0.81 (s, Me$_3$ on C-7); δ_C 132.00, 129.99, 68.26, 67.96, 66.91, 51.52, 36.98, 29.59, 24.00, 22.04 and 15.49 (Found: M$^+$, 190.1357. Calc. for $C_{13}H_{18}O$: *M*, 190.1353).

2-*Methoxy*-7,7-*dimethyl*-10-*oxatetracyclo*[6.3.0.0^{1,3}.0^{2,6}]-*undec*-4-*ene* **20**. δ_H(CDCl$_3$) 5.76 (dd, $J_{4,5}$ 5.9, $J_{4,3}$ 2.4, $J_{4,6}$ 0.4, 4-H), 5.58 (ddd, $J_{5,6}$ 2.8, $J_{5,3}$ 1.3, 5-H), 3.85 (d, $J_{11,11'}$ 9.2, 11-H), 3.80 (dd, $J_{9,9'}$ 9.6, 9-H), 3.57 (d, 9'-H), 3.55 (dd, 11'-H), 3.30 (s, OMe), 2.80 (d, 6-H), 2.03 (dd, 3-H), 1.08 (s, Me) and 0.85 (s, Me); δ_C 131.48, 129.66, 89.66, 67.67, 65.43, 63.96, 57.13, 51.38, 34.52, 30.15, 24.28 and 21.29 (Found: M$^+$, 206.1306. Calc. for $C_{13}H_{18}O$: *M*, 206.1302).

7-*Methoxy*-6,6-*dimethyl*-3-*oxatricyclo*[5.4.0.0^{1,5}]*undeca*-7,9-*diene* **30**. δ_H 6.26 (ddd, $J_{10,11}$ 9.9, $J_{10,9}$ 5.7, 10-H), 5.86 (ddd, $J_{9,8}$ 9.5, 9-H), 5.65 (d, with fine splittings, 8-H), 5.55 (d with fine couplings, 11-H), 4.00–3.20 (overlapping ms, 4-H, 4'-H, 6-H, 6'-H), 3.08 (s, –OMe), 1.36 (s, Me) and 1.35 (s, Me); *m*/*z* (M$^+$) 206.

5-*Oxapentacyclo*[5.5.1.0.0^{1,9}.0^{4,13}.0^{12,13}]*tridec*-10-*ene* **32**. δ_H 5.79 (dd, $J_{11,10}$ 5.6, $J_{11,12}$ 2.4, 11-H), 5.56 (dd, $J_{10,9}$ 2.8, 10-H), 3.97 (d, $J_{4,3}$ 4.2, 4-H), 3.84 (dd, $J_{6,6'}$ 9.0, $J_{6,7}$ 5.5, 6-H), 3.67 (d, 6'-H), 3.05 (br t, 9-H), 2.31 (qd, $J_{7,8}$ 5.5, $J_{7,8'}$ 5.5, $J_{7,6'}$ 1.6, 7-H), 2.27–2.16 (overlapping ms, 3'-, 8-, 8'-, 9-H), 2.04 (dd with fine couplings, $J_{2,2'}$ 8.0, $J_{2,3}$ 11.2, 2-H), 1.97 (dd, $J_{2',3}$ 12.5, 2'-H) and 1.38 (dddd, $J_{3,3'}$ 7.9, 3-H); δ_C 135.18, 128.83, 82.69, 74.48, 54.74, 52.42, 50.99, 39.97, 38.76, 33.48 and 26.18 (Found: M$^+$, 174.1041. Calc. for $C_{12}H_{14}O$ *M*, 174.1045).

2-*Oxapentacyclo*[5.4.2.0.^{4,11}.0^{6,8}.0^{7,11}]*tridec*-9-*ene* **40**. δ_H 5.68 (dd, $J_{9,10}$ 5.2, $J_{9,8}$ 2.0, 9-H), 5.51 (d, 10-H), 4.40 (d, $J_{1,12}$ 3.7, 1-H), 3.88 (t, $J_{4,3}$ 8.1, $J_{3,3'}$ 8.1, 3-H), 3.70 (dd, $J_{3',4}$ 10.1, 3'-H), 2.51 (ddd, $J_{4,5}$ 5.0, 4-H), 2.24–2.16 (ms, 12-, 13-H), 2.04–1.85 (ms, 5'-, 8-, 12'-, 13'-H) and 1.63 (br t, $J_{6,8}$ 5.6, $J_{6,5}$ 5.6, 6-H); δ_C 130.40, 129.49, 83.19, 72.04, 57.81, 56.52, 38.54, 38.12, 31.63, 28.74, 27.92 and 22.58 (Found: M$^+$, 174.1041. Calc. for $C_{12}H_{14}O$ *M*, 174.1045).

8,8-*Dimethyl-5-oxapentacyclo*$[5.5.1.0^{1,9}.0^{4,13}.0^{12,13}]$ *tridec-10-ene* **33**. δ_H 5.84 (dd, $J_{11,10}$ 5.7, $J_{11,12}$ 2.5, 11-H), 5.65 (dd, $J_{10,9}$ 2.9, 10-H), 3.95 (d, $J_{6,6'}$ 9.7, 6′-H), 3.94 (d, $J_{4,3}$ 3.6, 4-H), 3.70 (dd, 6-H), 2.68 (d, 9-H), 2.19 (2 × dd, $J_{2,2'}$ 7.8, $J_{2,3'}$ 8.2, $J_{2,3'}$ 6.2, 2-, 2′-H), 2.02 (d, $J_{7,6}$ 5.8, 7-H, dd, $J_{3,3'}$ 11.8, 3′-H), 1.97 (d, 12-H), 1.46 (ddd, 3-H), 1.19 (s, Me) and 0.87 (s, Me); δ_C 134.77, 129.04, 82.52, 70.01, 63.41, 63.22, 60.72, 55.38, 50.04, 37.60, 33.56, 28.93, 26.57 and 23.52 (Found: M^+, 202.1358. Calc. for $C_{14}H_{18}O$ *M*, 202.1356).

5,5-*Dimethyl-2-oxapentacyclo*$[5.4.2.0.^{4,11}.0^{6,8}.0^{7,11}]$*tridec-9-ene* **41**. δ_H 5.80 (dd, $J_{9,10}$ 5.1, $J_{9,8}$ 2.0, 9-H), 5.49 (d, 10-H), 4.33 (d, $J_{1,12}$ 4.1, 1-H), 4.01 (t, $J_{4,3}$ 8.7, $J_{3,3'}$ 8.7, 3-H), 3.84 (t, $J_{3',4}$ 8.7, 3′-H), 2.35 (t, 4-H), 2.29 (ddd, $J_{13,13'}$ 12.0, $J_{13,12}$ 9.1, 13-H), 2.17 (dd, $J_{12',12}$ 12.0, $J_{12',13'}$ 9.3, 12′-H), 1.97 (ddd, $J_{12,1}$ 4.1, 12-H), 1.90 (dd, 13′-H), 1.78 (d with fine couplings, $J_{8,6}$ 7.1, 8-H), 1.43 (d, 6-H), 1.14 (s, Me) and 1.03 (s, Me); δ_C 132.63, 131.81, 84.12, 81.96, 70.05, 66.86, 58.28, 45.96, 44.61, 38.09, 37.68, 29.59, 28.77 and 28.16 (Found: M^+, 202.1358. Calc. for $C_{14}H_{18}O$ *M*, 202.2956).

6-*Oxapentacyclo*$[6.5.1.0^{1,10}.0^{5,14}.0^{13,14}]$*tetradec*-11-*ene* **42**. δ_H 5.64 (dd, $J_{12,11}$ 5.5, $J_{12,13}$ 2.1, 12-H), 5.41 (ddd, $J_{11,10}$ 2.4, $J_{11.13}$ 0.80, 11-H), 3.96 (t, $J_{5,4}$ 3.8, $J_{5,4'}$ 3.8, 5-H, dd, $J_{7,8}$ 7.5, $J_{7,7'}$ 8.9, 7-H), 3.64 (dd, $J_{7',8}$ 3.8, 7′-H), 2.99 (q, $J_{10,9'}$ 2.6, 10-H), 2.39 (qd, $J_{8,9}$ 7.6, $J_{8,9'}$ 7.6, $J_{8,7}$ 7.6, $J_{8,7'}$ 3.8, 8-H), 1.90–1.80 (overlapping ms, 9-, 9′-H, 2-, 2′-H), 1.78 (br s, with fine couplings, 13-H), 1.63–1.52 (ms, 3-, 4-H), 1.35–1.23 (m, 4′-H) and 1.10–1.03 (m, 3′-H); δ_C 132.87, 128.65, 74.34, 72.17, 58.99, 49.06, 46.91, 44.29, 44.21, 42.74, 38.73, 26.87, 26.21 and 17.05 (Found: M^+, 188.1200. Calc. for $C_{13}H_{16}O$, *M*, 188.1197).

2-*Oxapentacyclo*$[5.4.3.0^{4,11}.0^{6,8}.0^{7,11}]$*tetradec-9-ene* **43**. δ_H 5.46 (dd, $J_{9,10}$ 5.4, $J_{9,8}$ 2.5, 9-H), 5.43 (d, 10-H), 4.16 (t, $J_{1,12}$ 8.2, $J_{1,12'}$ 8.2, 1-H), 3.39 (2 × t, $J_{3,4}$ 8.9, $J_{3,4'}$ 8.9, $J_{3,3'}$ 8.9, 3-H, 3′-H), 2.53 (quin, $J_{4,5}$ 8.9, $J_{4,5'}$ 8.9, 4-H), 1.96 (d with fine couplings, $J_{8,6}$ 5.2, 8-H) and 1.93–1.57 (ms, *J* 9.0 and 5.2, 5-, 5′-, 6-, 12-, 12′-, 13-, 13′-, 14-, 14′-H); δ_C 132.73, 132.47, 77.90, 73.31, 55.80, 44.20, 43.99, 39.41, 28.72, 25.38 and 19.02; *m*/*z* (M^+) 188.

6,6-*Dimethyl-9-oxatetracyclo*$[6.5.1.0^{2,5}.0^{10,14}]$*tetradec*-1(14),3-*diene* **44**. δ_H 5.57 (s, 3-, 4-H), 3.98 (t, $J_{8,8'}$ 8.7, $J_{8,7}$ 8.7, 8-H), 3.78 (dd, $J_{10,11'}$ 10.0, $J_{10,11}$ 6.2, 10-H), 3.71 (t, $J_{8',7}$ 9.0, 8′-H), 2.87 (d, $J_{2,5}$ 5.4, 2-H), 2.36 (t, 7-H), 2.03 (d, 5-H), 2.00–1.77 (overlapping ms, $J_{11,11'}$ 12.4, $J_{12,12'}$ 12.4, $J_{13,13'}$ 12.4, 11-, 11′-, 12-, 12′-, 13-, 13′-H), 1.10 (s, Me) and 0.85 (s, Me); δ_C 134.12, 130.87, 120.89, 117.60, 77.90, 67.44, 67.13, 52.76, 39.90, 28.91, 26.67, 26.36, 24.88 and 19.19; *m*/*z* (M^+) 216.

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