The Photo-Nazarov Cyclization of 1-Cyclohexenyl(phenyl)methanone Revisited − Trapping of the 2-Oxyallyl Intermediates by Olefins

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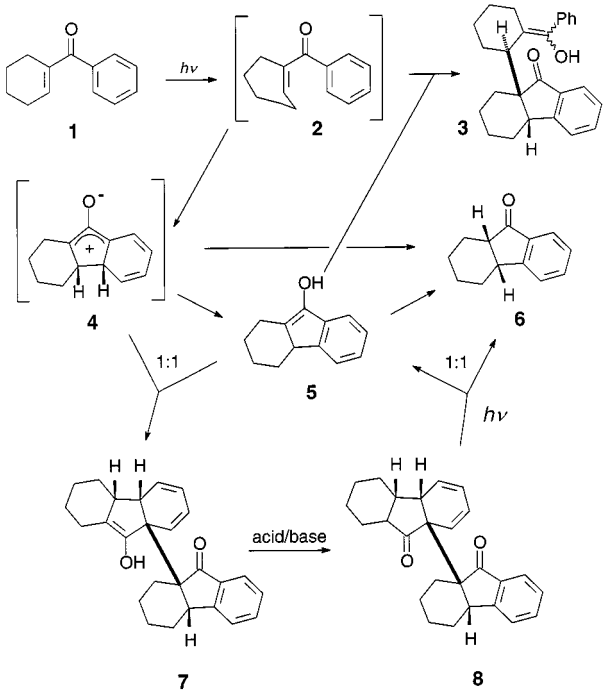
The photochemistry (> 300 nm) of 1-cyclohexenyl(phenyl)-methanone (**1**) in the presence of various monoolefins and cyclopentadiene (**9**) has been investigated. While (*Z*)-cyclooctene and 1-pentene were unreactive, styrene, (*E*)-cyclooctene, and diene **9** co-reacted upon irradiation of **1**. The reactions observed include [4 + 2] and [2 + 2] cycloadditions of the monoolefins to the primary photoproduct of **1** (which is the *trans* isomer **2**), and trapping reactions of the 2-oxyallyl compound **4** formed thermally from **2** as a secondary intermediate. The trapping reactions of **4** are ene-type additions of the olefins, analogous to those observed with the prototypical 2-oxyallyl compound **18** in purely thermal reactions, and involving a hydrogen transfer from **4** to olefin to give adducts **10**, **12**, **13**, **24**, and **25**. However, while **18** gives one single ene-type adduct with **9**, intermediate **4** displays two regioisomeric ene-type addition modes with **9**, both of which are concerted, albeit nonsynchronous. In the mode resulting in **10**, it is suggested that hydrogen transfer lags behind C–C bond formation, whereas the reverse holds for the mode affording **12** and **13**. For both major adducts, **10** and **12**, concerted formation requires *endo* orientations of the two π systems.

Introduction

The title reaction in aprotic media proceeds essentially as outlined in Scheme 1[1] (see Parts I[2] and II[3] of this series). Moreover, when the reaction was conducted in the presence of cyclopentadiene (**9**), the 2-oxyallyl[4] intermediate **4** was trapped by **9** to give adducts **10**, **12**, and **13** (Scheme 2[5]), in a ratio of 5:2.2:1 at room temperature.[2] Formation of **10** had precedents in the form of side reactions of the prototypical cyclopent-2-enylium-2-olate (**18**) with **9**, to give **19** (Scheme 3),[6] and also with a substituted derivative of **9**.[7] The formation of **12** and **13**, however, was novel. The mechanism of these addition reactions could not be elucidated unequivocally in our previous work. Two alternatives were discussed.[2] Firstly, in view of the fact that [4 + 3] cycloaddition was the dominant reaction of **18** with *cisoid* 1,3-dienes,[6,7] a primary formation of the [4 + 3] cycloadduct **15** was considered as one possibility. Driven by aromatisation, **15** might subsequently have rearranged to **10**, **12**, and **13**. Secondly, direct formation of **10**, **12**, and **13** from **4** and **9** − either in a concerted fashion or in two steps by way of the dipolar intermediate **16** or its corresponding diradical − appeared another possibility, while still another conceivable dipolar intermediate might be found in **17**. Like the mechanism, the scope of these addition reactions remained unclear, but extension to olefins other than **9** might hold synthetic promise. This situation prompted us to carry out this investigation into the following points: (i) the definitive structural assignment (“which is which”) of the two diastereomeric adducts **12** and **13**, (ii) the mechanisms of formation of **10**, **12**, and **13**, and (iii) extension of the trapping of **4** by **9** to olefins other than **9**.



Scheme 1. The photo-Nazarov reaction of 1-cyclohexenyl phenyl ketone (**1**) in aprotic solution[2,3]

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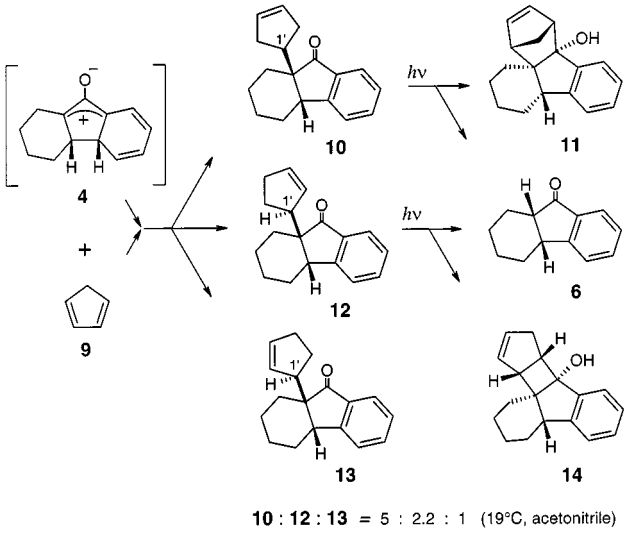
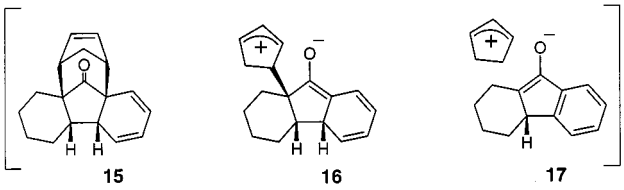
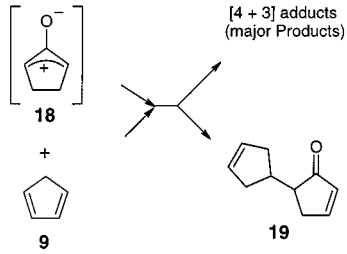




Scheme 2. Trapping of the 2-oxyallyl intermediate **4** with cyclopentadiene (**9**)[2] and photoreactions of adducts **10**[2] and **12**; structures **15**–**17** are conceivable (though rejected) intermediates en route to **10**, **12**, and **13**



Scheme 3. The prototypical addition of cyclopentadiene (**9**) to the 2-oxyallyl compound **18**[3,9]

Results and Discussion

Addition of Cyclopentadiene 9 to 4 − Structural Assignment of the Diastereomeric Adducts 12 and 13

The adduct of m.p. 38−41 °C[2] was subjected to single-crystal X-ray analysis, which found structure **12** (Figure 1). This structure was confirmed independently by the photocyclisation of the adduct to **14** (vide infra). It is thus necessary to reverse the previous − explicitly tentative − assignment of the two cyclopentadiene adducts to structures **12** and **13** in ref.[2]

Irradiation of the Pentadeuteriophenyl Methanone 1-d_5 in the Presence of 9

Ketone **1-d_5** was irradiated in acetonitrile in the presence of **9** in the same manner as **1**,[2] to give deuterated derivatives of the products shown in Scheme 1 and Scheme 2. In place of adducts **11** and **12**, the deuterated products **11-d_5** and **12-d_5** were isolated (Scheme 4); since irradiation had been carried to complete consumption of **1-d_5**, compounds **10-d_5** and **13-d_5** had undergone secondary photolysis (Scheme 2). NMR spectroscopy unequivocally established the positions of the non-aromatic D atoms in both. In analogy to the formation of **11** from **10**,[2] **11-d_5** must have been formed from **10-d_5** under the irradiation conditions. Hence, the position of the non-aromatic D atom in **10-d_5** follows from its position in **11-d_5**. At this point it is useful to remember that adducts **10**, **12**, and **13** are not interconverted under the irradiation and workup conditions.

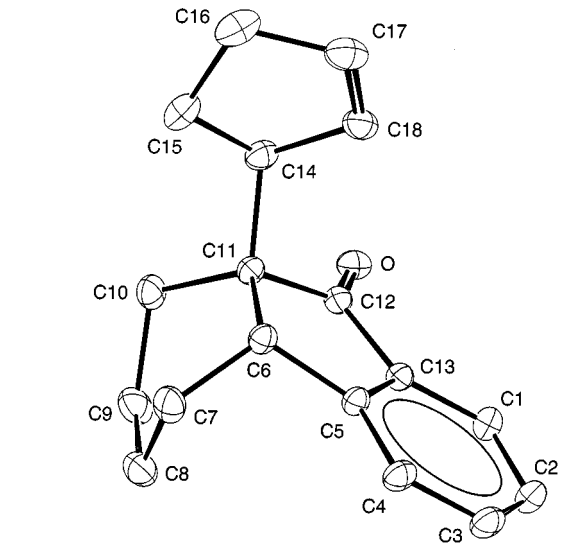
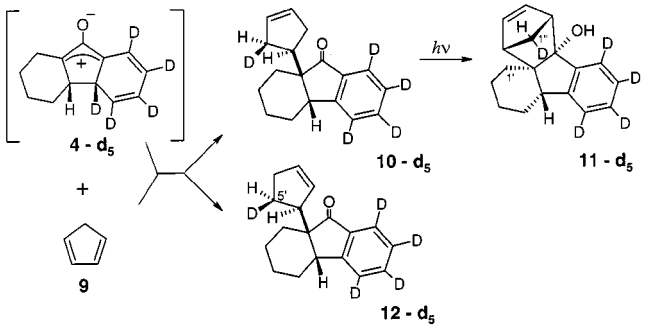


Figure 1. Molecular structure of **12** as found by X-ray crystallography; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level



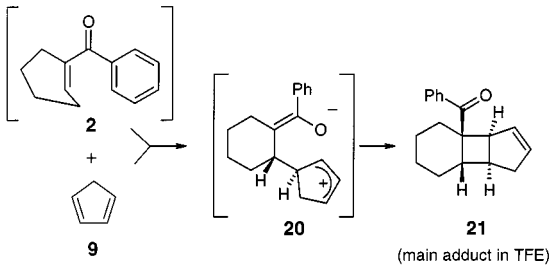
Scheme 4. Trapping of the oxyallyl intermediate **4-d_5** with cyclopentadiene (**9**) and subsequent photocyclization of adduct **10-d_5**

In order to determine relative H/D isotope effects associated with the formation of the individual photoproducts, we irradiated **1** and **1-d_5** under identical conditions in parallel experiments, in acetonitrile and in the presence of **9**, and compared the relative yields of products by 400-MHz ^{1}H NMR analysis of the product mixtures. In order to minimise the secondary photoreaction − (formation of **11** and **11-d_5**) − the degree of photoconversion was kept minimal. Not surprisingly, the relative yields of the three [4 + 2]

adducts of **9** with **2**[2] (not shown in the Schemes) did not differ from those of **9** with **2-d$_5$**. Thus, the H/D isotope effects associated with the formation of these adducts are negligible. Ring closure **2-d$_5$** → **4-d$_5$**, however, was slower than formation of the three [4 + 2] adducts by a factor of 1.3 relative to the undeuterated case. Thus, there is a noticeable secondary isotope effect associated with the ring closure **2-d$_5$** → **4-d$_5$**. The yield of **10-d$_5$** (including a small amount of **11-d$_5$**) relative to **6-d$_5$** + **8-d$_{10}$** was lower than that of **10** (including a small amount of **11**) relative to **6** + **8** by a factor of 3.9 (**3**, **5** and **7**, and deuterated analogues could be neglected). As a consequence, the primary H/D isotope effect for the formation of **10** from **4** + **9** must be larger than 3.9, since the conversion **4** → → (**6** + **8**) can also be expected to involve a significant primary H/D isotope effect. Similarly, the primary isotope effect for the formation of **12** from **4** + **9** was found to be larger than 6.2.

Irradiation of 1 and 1-d$_5$ in the Presence of 9 in 2,2,2-Trifluoroethanol and of 1 in Toluene

In order to explore the influence of solvent polarity on the relative rates of adduct formation, **1** was irradiated in the presence of **9** in the nonpolar toluene and in 2,2,2-trifluoroethanol (TFE), which is more powerfully ionising than the acetonitrile previously used as solvent. In toluene (upon 46% conversion), the following products were isolated: 76.8% of the [4 + 2] adducts of **9** with **2** (vide supra), 0.8% of **21**, a hitherto overlooked [2 + 2] adduct of **9** with **2** (Scheme 5), 1.6% of **3**, 5% of **6**, 2.5% of **8**, 9.7% of **10**, and 1.1% of **12**. Irradiation of **1** without added **9** in TFE should lead exclusively to **5** + **6**, in analogy to the result obtained in methanol,[2] due to catalysis of the reactions **2** → **4** and **4** → **5** by the hydroxy proton. In the presence of **9** in TFE under the same conditions as in toluene, compound **1**, after 43% conversion, gave 7.6% of the [4 + 2] adducts of **9** with **2** (vide supra), 10.2% of **21**, 46.3% of the anticipated main product **6**, 22.8% of **12**, and 6.6% of **13**. Remarkably, **10** and **11** were absent.



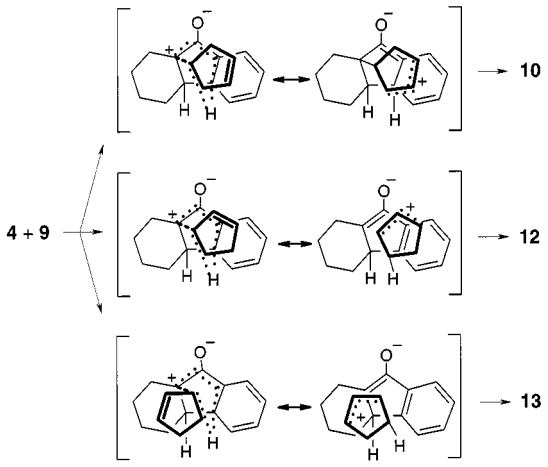
Scheme 5. [2 + 2] addition of cyclopentadiene (**9**) to the primary photo-Nazarov product **2**

Mechanisms of Formation of 10, 12, 13, and 21

The increase by a factor of 129 in the rate of formation of **21** relative to that of the [4 + 2] adducts on going from toluene to TFE is in line with a formation of **21** via the 1,4-dipole **20**, in contrast to the concerted formation of the [4 + 2] adducts by way of a much less polar transition state. There is a similarly dramatic increase in the rate of formation of **12** and **13**, relative to that of **10**. When the pentadeuteriophenyl analogue **1-d$_5$** was irradiated in the presence of **9** in TFE, we obtained a result corresponding to that obtained with **1**, as was to anticipated. However, the fact that **12-d$_5$** was formed in place of a **12-d$_4$** product (lacking the non-aromatic D atom) is not trivial. If **12** were formed by a reaction between **5** and **9**, then **5-d$_5$** would quickly have exchanged its OD group for OH by fast proton exchange with the solvent TFE and hence would have produced **12-d$_4$** upon reaction with **9**. Thus, formation of **12** from **5** and **9** is ruled out.

The position of the non-aromatic D atom in **10-d$_5$** does not preclude the possibility that **10** might have been formed by way of **15**. When the irradiation of **1** was carried to partial conversion only, so that **15** should be protected against light by **1** (note that excited **1** is not quenched by 1,3-dienes such as **9**), we could neither detect any olefinic ^{1}H NMR signals attributable to **15** in the crude reaction mixture nor isolate any **15** by chromatography. A thermal rearrangement, **15** → **10**, being symmetry-forbidden, would have to proceed in two steps through a 1,5-dipole or diradical. The activation energy expected for such a reaction[8] should amply suffice to render **15** thermally stable at room temperature. Thus, if **15** had been formed, we should have observed it. Moreover, formation of **15** should not be subject to an H/D isotope effect as high as > 3.9, which we observe for the formation of **10**. Since direct formation of **10** from **5** and **9** can be rejected on grounds of the expected reactivity of the reactants (which would favour formation of **12** and **13** rather than **10**), **10** must be formed directly from **4** and **9**, and we have to address the question of whether this reaction is concerted or two-step by way of **16** (or the corresponding diradical). In an investigation of the reactions of the prototypical 2-oxyallyl compound **18** with olefins and 1,3-dienes in TFE,[9] we concluded that the symmetry-allowed ene-type addition exemplified by the reaction **9** + **18** → **19** and dubbed "ene-type 1" addition, should have a transition state very close to a 1,5-dipole (as exemplified by **16**) with a small but definite concertedness. Such concertedness should increase dramatically when the second "step" in the nonsynchronous concerted addition − the hydrogen transfer − involved formation of an aromatic ring (as in the formation of **10**), since the more concerted the reaction, the more it benefits from the high energy bonus due to attaining aromaticity. Thus, we conclude that the formation of **10** from **4** and **9** is quite strongly concerted. The same conclusion also follows from the primary H/D isotope effect of > 3.9. The alternative explanation for this isotope effect, a rapidly established equilibrium between **4** + **9** and **16** (or the corresponding diradical) followed by a rearrangement **16** → **10** in the rate-determining step, can be dismissed, since in the closely related case of **9** + **18**, the first step in the two-step diene addition is irreversible by a very high energy margin.[9,10] As the position of the non-aromatic D atom in **10-d$_5$** shows, the concerted formation

of **10** involves *endo* orientations of the "nonreacting" C=C double bond in **9** and the "nonreacting" oxyallyl CCO moiety in **4** (Scheme 6).



Scheme 6. Proposed transition states for the ene-type additions of **9** to **4**; the left-hand formulae illustrate the concerted nature of the additions; the right-hand formulae, depicting open-chain dipolar resonance structures (cf. **16** and **17**) significantly contributing to the transition states, illustrate the nonsynchronous nature of the additions

The position of the non-aromatic D atom in **12-d$_5$** precludes the possibilities that **12** be formed through **16** (or the corresponding diradical) or via **15**. Formation of **12** from **5** and **9** has been ruled out above, so three possibilities for the formation of **12** remain: directly from **4** and **9**, either in a concerted fashion or via the ion pair **17** (or the corresponding radical pair). The very strong acceleration of the formation of **12** and **13** relative to **10** on increasing the solvent ionising power from acetonitrile to TFE points to the route through **17** in TFE. However, the regiospecificity, documented by the position of the non-aromatic D atom in **12-d$_5$**, rules out equivalence of the two ends of the allylic cation in **17**. It can only be reconciled with a symmetry-allowed concerted reaction, with **17** merely approximating the transition states of concerted but non-synchronous pathways to **12** and **13**. The much stronger increase in the rates of formation of **12** and **13**, relative to that of **10**, with solvent-ionising power means that the degree of concertedness for the former is less than for the latter, with the dipolar resonance structure contributing more to the transition state in the former case than in the latter. Inspection of the dipolar resonance structures (**17** and **16**) suggests a possible cause for this: a much lower energy for **17** than for **16**, due to the presence of a benzene ring in the former but not in the latter. Since the **12/13** ratio, in contrast to the **12/10** ratio, does not vary strongly with solvent polarity, the mechanisms of formation of **12** and **13** ought to be similar, the difference being that in the transition state the "nonreacting" C=C double bond site of **9** and the "nonreacting" oxyallyl CCO moiety of **4** are *endo*-oriented en route to **12** and *exo*-oriented in the case of **13** (Scheme 6).

Irradiation of 10 and 12

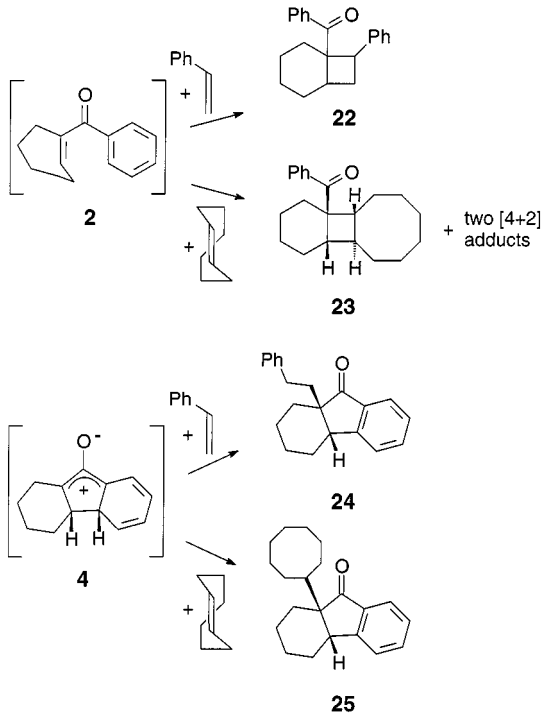
Compound **10** on irradiation, even at high concentrations of **9** and low concentrations of **1**, is converted into **6** and **11** in a 1:1.5 ratio.[2] Compound **12** is photostable under these conditions, but, when irradiated alone in acetonitrile, it was converted into a complex mixture from which **6** and **14** were isolated in 30.6% and 6.5% yields, respectively. According to the structures of these products, both transformations involve Norrish type-II 1,5-hydrogen abstractions: an expected result. The photoreaction of **12** is obviously quenched by the diene **9** and thus proceeds from the excited triplet state, as is normally the case in Norrish type-II reactions of phenyl ketones.[11] The photoreaction of **10**, however, is not quenched by **9**. Since excited singlet states of phenyl ketones are extremely short-lived, this result points to a particularly rapid 1,5-hydrogen abstraction by the excited carbonyl group of **10**, whatever the spin multiplicity of the latter. Indeed, the energetically most favourable conformation of ground state **10** has the target hydrogen atom ideally placed for abstraction in the carbonyl plane and close to the oxygen atom. The allylic radical in the moment of formation by the hydrogen abstraction has its other end placed above this plane, corresponding to an elongated C−C single bond between it and the other radical centre; collapse of this elongated bond gives **11**.

Irradiation of 1 in the Presence of Styrene − Addition of Styrene to 4

Irradiation of **1** to 84.7% conversion, in acetonitrile in the presence of 1.8 M styrene, gave three [2 + 2] adducts of constitution **22** in 2.3, 8.7, and 2.1% yields (based on unrecovered **1**), 40.5% (according to ^{1}H NMR analysis of the reaction mixture; isolated yield 25.7%) of the adduct **24**, 1.1% of an open-chain adduct [2-(2′-styryl)cyclohexyl phenyl ketone], 13.7% of **6**, and 18.7% of **8** (Scheme 7). The three adducts **22** are analogous to **21**; **24** is analogous to **10**.

Irradiation of 1 in the Presence of (*E*)-Cyclooctene − Addition of (*E*)-Cyclooctene to 4

In the presence of 1.0 M (*E*)-cyclooctene in acetonitrile, compound **1** gave the two Diels−Alder [4 + 2] adducts of (*E*)-cyclooctene to **2** (6.7 and 1.3%), 10.9% of the [2 + 2] adduct **23**, 29.3% of the adduct **25**, 3.3% of a cyclobutanol formed from **25** by a Norrish type-II photocyclization, 8.1% of **6**, and two diastereomeric oxetanes formed by photoaddition of (*E*)-cyclooctene to **6** (2.0 and 0.2%) (yields based on unrecovered **1** at 66.1% conversion) (Scheme 7). Compound **23** is analogous to **21**, and **25** analogous to **10**, **12**, and **13**. The mode of formation of secondary photoproducts was verified by irradiation of **25** alone, and of **6** in the presence of (*E*)-cyclooctene. When the photoconversion of **1** was driven to 100%, the proportion of secondary photoproducts among the products increased strongly. According to analytical experiments (see Table 1), the com-



Scheme 7. Trapping of the primary photoproduct, (*E*)-cyclohexenyl phenyl ketone **2**, and of the oxyallyl intermediate **4** with styrene and (*E*)-cyclooctene

bined yield of the [4 + 2] adducts + **23**, relative to the combined yield of **6** + **25** + secondary products, was roughly proportional to the concentration of (*E*)-cyclooctene, as was to be expected. The yield of **23** relative to that of the two [4 + 2] adducts, however, did not change within error limits upon a fourfold increase of (*E*)-cyclooctene concentration, indicating that **23**, like the [4 + 2] adducts, originates from an addition of (*E*)-cyclooctene to **2**.

When **1-d$_5$** was used in place of **1**, a **25-d$_5$** derivative was obtained. This product was a ca. 1:1 mixture of two diastereomers, which differed only in the positions of the nonaromatic D atom in the cyclooctane ring. Both positions are *seq-trans* vicinal to the exocyclic C−C bond (for details see Exp. Sect., last but one paragraph). Thus, the formal addition of hexahydrofluorenone to the C=C bond of (*E*)-cyclooctene is cleanly suprafacial, in line with a concerted addition of (*E*)-cyclooctene to **4** in analogy to the formation of **10**.

Irradiation of 1 in the Presence of Other Olefins

In contrast to **9**, styrene, and (*E*)-cyclooctene, the olefins (*Z*)-cyclooctene and 1-pentene did not co-react when present during irradiation of **1** in acetonitrile. The irradiation of **1** in the presence of the highly reactive, electron-rich olefin ethyl vinyl ether has been described by us previously.[12]

Conclusion

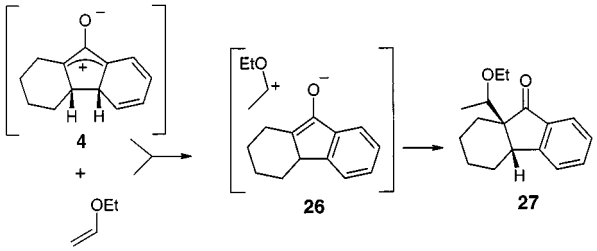
Similarly to what was found for the prototypical cyclopent-2-enylium-2-olate (**18**, Scheme 3),[9] the 2-oxyallyl compound **4**, which is formed as an intermediate in the course of the irradiation of **1**, gives ene-type addition reactions with 1,3-cyclopentadiene (**9**), styrene, and (*E*)-cyclooctene, but not with (*Z*)-cyclooctene, nor with 1-pentene. Thanks to the readier hydrogen abstraction from **4**, as compared to **18**, in the course of this ene-type addition, the addition is more strongly concerted with **4** than it is with **18**. While the addition of **9** to **18** highly regioselectively affords only **19**,[9] the reaction between **4** and **9** unselectively produces both **10** (which is analogous to **19**) and **12** + **13**, in what appear in each case to be concerted reactions. The addition producing **12** + **13** differs from the one producing **10** in that it has a much more strongly polar transition state in which hydrogen abstraction precedes C−C bond formation, whereas the reverse sequence holds for the formation of **10**, analogously to the formation of **19**.[9] For the two major adducts **10** and **12**, the addition reactions involve *endo* orientations of the two π systems.

In the light of the mechanism of formation of **12** as established in the present work, it now appears that the adduct **27** obtained upon irradiation of **1** in the presence of ethyl vinyl ether [12] is probably formed from **4** and ethyl vinyl ether via a transition state resembling **26** (Scheme 8) analogously to the formation of **12**, rather than from **5** and ethyl vinyl ether as was suggested in our previous paper[12] on grounds of precedents.

Table 1. Analytical irradiation of **1** in the presence of (*E*)-cyclooctene

Run	(*E*)-Cyclooctene [M][a]	[**23**]/[**A**[b]]	[**A**]/[**25**]	[**23**]/[**25**]	[**25**]/[**6** + **B**[c]]	[**23** + **A**]/[**6** + **25** + **B**]
1	0.7	1.52	0.105	0.16	3.24	0.203
2	0.7	1.21	0.116	0.14	3.74	0.202
3	1.4	1.81	0.138	0.25	5.44	0.328
4	1.4	1.79	0.140	0.25	4.78	0.323
5	2.8	1.69	0.295	0.50	5.93	0.680
6	2.8	1.87	0.267	0.50	4.55	0.627

[a] 0.1 M **1** in acetonitrile; six parallel runs in a merry-go-round apparatus at λ >300 nm for 4 h. − [b] **A** ≡ two [4 + 2] Diels−Alder adducts of **9** to **2**. − [c] **B** ≡ two oxetanes (secondary photoproducts from **6**).



Scheme 8. Proposed ion-pair-like (**26**) transition state for the addition of ethyl vinyl ether to 2-oxyallyl compound **4**

Experimental Section

General Methods: See our earlier publications.[2,3] As described in these, the molecular structures of new compounds encountered in the present work could be fully elucidated by the use of 400-MHz ^{1}H NMR techniques, including ^{1}H,^{1}H spin decoupling and NOE (Nuclear Overhauser Effect) experiments where suitable, ^{13}C BB (Broad Band decoupling), ^{13}C DEPT (Distortionless Enhancement by Polarisation Transfer), and CH correlation spectroscopy.

Crystal Data Collection and Refinement of the Structure of 12: Crystal system: monoclinic; space group: *Cc* (no. 9); a = 7.3572(6) Å, b = 15.2850(12) Å, c = 12.4239(10) Å; β = 100.696(3)°; V = 1372.85(19) Å^3; Z = 4; $\rho_{calcd.}$ = 1.221 g cm^{-3}; F(000) = 544 e; λ (Mo-K_α) = 0.71073 Å; T = 100 K; $2\theta_{max}$ = 66.16°; reflections collected/unique: 6780/2867 [R(int) = 0.1012]. The structure was solved by direct methods and refined by full-matrix, least-squares methods on F^2 with 2 restraints, 172 parameters (SHELX-97). Hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were refined anisotropically. R_1 = 0.0622 [$I > 2\sigma(I)$], wR_2 = 0.1555, Goodness of fit on F^2 = 1.021; max./min. residual density = 0.9/−0.3 e·Å^{-3}. Crystallographic data (excluding structure factors) for **12** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155324. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

(1′*S,4a*S**,5′*S**,9a*R**)-9a-(5′-Deuteriocyclopent-2′-enyl)-1,2,3,4,4a,9a-hexahydro-5,6,7,8-tetradeuteriofluoren-9-one (12-d$_5$) and (1*S**,1′′*R**,4*R**,4a*S**,9*S**,9a*R**)-9,9a-Butano-1,4-(monodeuteriomethano)-1,4,4a,9a-tetrahydro-5,6,7,8-tetradeuterio-9*H*-fluoren-4a-ol (11-d$_5$):** These compounds were prepared from the pentadeuteriophenyl ketone **1-d$_5$**[2] analogously to the preparation of **12** and **11** from **1**.[2] Comparison of the ^{1}H and ^{13}C NMR spectra of **12**[2] and **12-d$_5$** shows that the H atom with signal at δ = 1.68 on C-5′ (δ = 25.3) of **12** is replaced by D in **12**-d$_5$ (the atom numbering is different from that employed in Figure 1!). Similarly, the H atom with signal at δ = 1.25 on C-1′′ (δ = 44.0) in **11**, which shows a strong mutual ^{1}H,^{1}H NOE enhancement with 9-H,[2] is replaced by D in **11-d$_5$**. No further differences in the nonaromatic part are observed in the spectra of either compound.

Phenyl{(1*R,2*R**,7*S**,8*S**)-tricyclo[6.3.0.0^{2,7}]undec-10-en-2-yl}-methanone (21):** Compound **1** (2.0 g, 10.75 mmol), dissolved in a deaerated mixture of 2,2,2-trifluoroethanol (TFE, 150 mL) and freshly distilled cyclopentadiene (**9**) (23 g), was irradiated at room temp. under argon with light of λ > 300 nm from a concentrically placed 125-W high pressure mercury lamp as described previously.[2] After 1 h, conversion of **1** had reached 43% and irradiation was discontinued. After evaporation of TFE and **9**, the residue was chromatographed with pentane + 2% ether. Sequence of elution: [4 + 2] adducts, **21**, **12**, **1**, **6**.

Compound 21: ^{1}H NMR ($CDCl_3$): δ = 0.99 (qt; J = 3 × 13.1 and 2 × 3.0 Hz; 1 H), 1.39 and 1.49 (2 m; 1 H each), 1.61 (m; 3 H), 1.97 (td; J = 2 × 14.0 and 3.4 Hz; one 3-H), 2.12 (dddd; J = 16.7, 2.7, 2.4, and 2.0 Hz; one 9-H), 2.39 (m; one 3-H), 2.42 (ddtd; J = 16.7, 7.8, 2 × 2.4, and 2.0 Hz; one 9-H), 2.60 (ddd; J = 7.8, 7, and 2 Hz; 7-H), 2.77 (td; J = 2 × 7.8 and 6.2 Hz; 8-H), 3.50 (ddtd; J = 6.2, 2.7, 2 × 2.4, and 2.0 Hz; 1-H), 5.38 (dq; J = 5.4 and 3 × 2.4 Hz; 11-H), 5.70 (dq; J = 5.4 and 3 × 2.0 Hz; 10-H), 7.41 (m; two *m*-phenyl H), 7.49 (m; *p*-phenyl H), 7.91 (d; J = *8 Hz*; two *o*-phenyl H). − ^{1}H,^{1}H NOE enhancements ($CDCl_3$): *o*-phenyl-H/1-H, *o*-phenyl-H/11-H, *o*-phenyl-H/two 3-H, 1-H/8-H, 1-H/3-H at δ = 1.97, 3-H at δ = 1.97/8-H, 7-H/9-H at δ = 2.12. − ^{13}C NMR ($CDCl_3$): δ = 21.9 and 22.1 (C-4, -5), 24.9, 34.4, 35.5, 38.4, 40.4, 53.7 and 59.3 (C-6, -3, -8, -9, -7, -2, and -1, respectively), 128.4 (2 *m*-phenyl-C), 129.1 (2 *o*-phenyl-C), 129.9 (C-11), 132.3 (*p*-phenyl-C), 134.1 (C-10), 134.9 (*ipso*-phenyl-C), 203.9 (C=O).

(1*R,2*S**,7*S**,10*S**,11*S**)-8,9-Benzotetracyclo[9.3.0.0^{2,7}.0^{2,10}]-tetradec-13-en-10-ol (14):** A deaerated solution of **12** (103 mg, 0.4 mmol) in acetonitrile (40 mL) was irradiated with light of λ > 300 nm under argon at room temp. until full conversion (9 h). After evaporation of the solvent, the residue was chromatographed with pentane + 3% ether. Sequence of elution: 10.1 mg of unidentified mixtures, 23.3 mg (30.6%) of **6**, 8.4 mg (6.5%) of **14**, 61.1 mg of unidentified mixtures.

Compound 14: ^{1}H NMR ($CDCl_3$): δ = 1.19 (dddd; J = 13, 11, 10.3, and 4 Hz; one 6-H), 1.3 (m; 3 H), 1.42 (ddd; J = 14, 9.5, and 4 Hz; one 3-H), 1.51 (m; 1 H), 1.68 (ddd; J = 14, 7, and 4 Hz; one 3-H), 1.94 (variable; bs; OH), 2.00 (ddddd; J = 13, 6, 4, 3.5, and 1.5 Hz; one 6-H), 2.46 (ddt; J = 17.5, 10.5, and 2 × 2.3 Hz; one 12-H), 2.57 (dtd; J = 7.5, 2 × 3.0, and 1.0 Hz; 1-H), 2.80 (ddtd; J = 17.5, 3.8, 2 × 3.0, and 2.3 Hz; one 12-H), 2.88 (ddd; J = 10.5, 7.5, and 3.8 Hz; 11-H), 2.91 (dd; J = 10.3 and 6.0 Hz; 7-H), 5.70 (dtd; J = 5.6, 2 × 3.0, and 2.3 Hz; 14-H), 5.95 (dtd; J = 5.6, 2 × 2.3, and 1.0 Hz; 13-H), 7.24 (m; 3 H), 7.37 (m; 1 H). − ^{1}H,^{1}H NOE enhancements ($CDCl_3$): 1-H/7-H, 3-H at δ = 1.42/14-H. − ^{13}C NMR ($CDCl_3$): δ = 21.3 and 21.8 (C-4, -5), 23.4 (C-3), 31.5 (C-6), 32.9 (C-12), 48.1 (C-11), 50.7 (C-7), 51.7 (C-1), 54.4 (C-2), 83.8 (C-10), 123.4, 124.3, 127.8, and 128.2 (4 CH), 130.8 (C-14), 134.6 (C-13), 147.7 and 147.9 (C-8, -9).

Irradiation of 1 in Acetonitrile in the Presence of Styrene: Compound **1** (1.0 g, 5.37 mmol), dissolved in a deaerated mixture of acetonitrile (40 mL) and freshly distilled styrene (10 g), were irradiated as described in the preceding sections for 70 min, to 84.7% conversion. Still under argon, *p*-toluenesulfonic acid (10 mg) was added, immediately bleaching the yellow solution (**7** → **8**). After evaporation of the acetonitrile and most of the styrene, the residue was chromatographed with pentane + 2% ether. Sequence of elution: styrene, **22** (unknown stereochemistry, 2.3%), (1*S**,6*S**,8*S**)-**22** (8.7%), (1*R**,6*S**,8*S**)-**22** (2.1%), [2-(2′-styryl)cyclohexyl](phenyl)methanone, **1**, **24**, **8**, **6**.

Phenyl{8-phenylbicyclo[4.2.0]oct-1-yl}methanones (22)

(1*S,6*S**,8*S**)-22:** ^{1}H NMR ($CDCl_3$): δ = 0.90 (qdd; J = 3 × 13.3, 5.6, and 3.6 Hz; 1 H), 1.40 (m; 1 H), 1.45 and 1.76 (2 m; 1 CH_2), 1.60 (dm; J = 12.4 Hz; one 5-H), 1.85 (ddd; J = 13.4, 12.4, and 3.4 Hz; one 2-H), 2.12 (tdd; J = 2 × 12, 7.3, and 3.1 Hz; 6-H),

2.23 (ddd; J = 9.4, 7.3, and 6.4 Hz; one 7-H), 2.24 (dtd; J = 12.4, 2 × 12, and 4.1 Hz; one 5-H), 2.33 (dt; J = 12.4 and 2 × 3.0 Hz; one 2-H), 2.99 (ddd; J = 12, 10.8, and 9.4 Hz; one 7-H), 3.70 (dd; J = 10.7 and 6.4 Hz; 8-H), 7.03 (m; 3 phenyl-H), 7.10 (m; 2 phenyl-H), 7.17 (m; 5 phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = 23.2 and 26.9 (C-3, -4), 23.7 (C-5), 32.2 (C-7), 39.1 (C-2), 45.7 (C-6), 55.1 (C-8), 64.3 (C-1), 127.0 (*p*-phenyl-C), 127.1, 128.2, 128.6, and 128.7 (4 × 2 phenyl-C), 130.7 (*p*-phenyl-C), 138.2 and 139.7 (2 *ipso*-phenyl-C), 205.4 (C=O).

(1*R,6*S**,8*S**)-22:** ^{1}H NMR ($CDCl_3$): δ = 0.98 (qdd; J = 3 × 13.3, 5.6, and 3.6 Hz; 1 H), 1.45 (m; 2 H), 1.62 (m; 1 H), 1.62 and 1.71 (2 m; two 5-H), 1.87 (m; two 2-H), 2.04 (ddd; J = 10.2, 8, and 7.8 Hz; one 7-H), 2.31 (td; J = 2 × 10.8 and 10.2 Hz, one 7-H), 2.95 (dddd; J = 10.8, 8, 6.7, and 1.4 Hz; 6-H), 3.62 (dd; J = 10.8 and 7.8 Hz; 8-H), 7.21 (d; J = 7.3 Hz; 2 *o*-phenyl-H), 7.29 (m; *p*-phenyl-H), 7.31 (m; 4 *m*-phenyl-H), 7.43 (t; J = 2× 7.3 Hz; *p*-benzoyl-H), 7.51 (d; J = 7.8 Hz; 2 *o*-benzoyl-H). − ^{1}H,^{1}H NOE enhancements ($CDCl_3$): *o*-benzoyl-H/2-H, *o*-benzoyl-H/5-H at δ = 1.71, *o*-benzoyl-H/6-H, *o*-benzoyl-H/8-H, 6-H/8-H. − ^{13}C NMR ($CDCl_3$): δ = 21.3 and 21.4 (C-3 and -4), 25.2 (C-7), 25.4 (C-5), 25.8 (C-2), 32.3 (C-6), 45.3 (C-8), 57.0 (C-1), 126.7 (*p*-phenyl-C), 127.9 and 128.0 (each 2 *m*-phenyl-C), 128.6 (2 *o*-benzoyl-C), 129.5 (2 *o*-phenyl-C), 131.4 (*p*-benzoyl-C), 136.8 and 139.7 (2 *ipso*-phenyl-C), 206.8 (C=O).

(4a*R,9a*S**)-9a-(2-Phenylethyl)-1,2,3,4,4a,9a-hexahydrofluoren-9-one (24):** M.p. 65 °C. − MS (EI and CI): m/z = 290 [M^+]. − ^{1}H NMR ($CDCl_3$): δ = 1.27 (m; 2 H), 1.48 and 1.57 (2 m; 1 H each), 1.58 and 1.76 (2 m; 1 CH_2), 1.83 and 1.99 (2 m; 1 CH_2), 1.89 and 2.00 (each a d-quasi-t; J = 13.8 and 2 × 8.6 Hz; two 1′-H), 2.49 (quasi-t; J = 2 × 8.6 Hz; two 2′-H), 3.29 (t; J = 2 × 5.5 Hz; 4a-H), 7.14 (m; 3 phenyl-H), 7.23 (m; 2 phenyl-H), 7.37 (t; J = 2 × 7.4 Hz; 7-H), 7.47 (d; J = 7.6 Hz; 5-H), 7.59 (td; J = 2 × 7.4 and 1.1 Hz; 6-H), 7.77 (d; J = 7.6 Hz; 8-H). − ^{13}C NMR ($CDCl_3$): δ = 20.3, 20.5, 26.7, and 31.0 (4 CH_2), 31.1 (C-2′), 38.9 (C-1′), 43.2 (C-4a), 53.3 (C-9a), 124.2 (C-8), 124.8 (C-5), 125.8 (*p*-phenyl-C), 127.4 (C-7), 128.3 (2 *m*-phenyl-C), 128.4 (2 *o*-phenyl-C), 134.5 (C-6), 136.0 (*ipso*-phenyl-C), 142.4 (C-8a), 156.7 (C-4b), 210.4 (C-9).

Irradiation of 1 in Acetonitrile in the Presence of (*E*)-Cyclooctene: Compound **1** (1.0 g, 5.37 mmol), dissolved in a deaerated mixture of acetonitrile (45 mL) and freshly distilled (*E*)-cyclooctene (5.5 g), was irradiated as described[2] for 1 h and to 66.1% conversion. After evaporation of the acetonitrile and most of the (*E*)-cyclooctene, the residue was chromatographed with pentane + 1% ether. Sequence of elution: (*E*)-cyclooctene, major [4 + 2] adduct (6.7%), minor [4 + 2] adduct (1.3%), **23**, major oxetane (secondary photoproduct from **6**), **25**, **1**, minor oxetane (secondary photoproduct from **6**), **6**, cyclobutanol isomer of **25** (secondary photoproduct from **25**).

(6a*S,12a*R**,12b*S**)-5-Phenyl-1,3,4,6a,7,8,9,10,11,12,12a,12b-dodecahydro-2*H*-6-oxacycloocta[*a*]naphthalene (Major [4 + 2] Adduct):** ^{1}H NMR ($CDCl_3$): δ = 1.1−1.95 (m; 18 H), 1.85 (td; 2 × 13.1 and 4.1 Hz; one 4-H), 2.05 (m; 12a-H and 12b-H), 2.50 (ddt; J = 13.1, 4.0, and 2 × 2.0 Hz; one 4-H), 3.87 (ddd; J = 10.2, 5.6, and 3.1 Hz; 6a-H), 7.23 (tt; J = 2 × 7.2 and 2 × 1.6 Hz; *p*-phenyl H), 7.30 (t; J = 2 × 7.2 Hz; 2 *m*-phenyl-H), 7.36 (dd; J = 7.2 and 1.6 Hz; 2 *o*-phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = 21.9, 25.7, 26.7, 27.0, 27.3, 28.2, 28.9, 29.1, and 29.9 (9 CH_2) 30.7 (C-4), 39.6 (C-12b), 42.3 (C-12a), 76.0 (C-6a), 114.1 (C-4a), 127.4 (*p*-phenyl-C), 127.7 (2 *m*-phenyl-C), 129.7 (2 *o*-phenyl-C), 136.7 (*ipso*-phenyl-C), 145.6 (C-5).

(6a*S,12a*R**,12b*R**)-5-Phenyl-1,3,4,6a,7,8,9,10,11,12,12a,12b-dodecahydro-2*H*-6-oxacycloocta[*a*]naphthalene (Minor [4 + 2] Adduct):** ^{1}H NMR ($CDCl_3$): δ = 0.96 (qd; J = 3 × 13.3 and 3.6 Hz; 1 H), 1.33 (m; 2 H), 1.4−1.94 (m; 14 H), 1.46 and 1.75 (2 m; 12a-H and 12b-H), 2.00 (m; 1 H), 2.12 (m; 1 H), 2.57 (dq; J = 13.8 and 3 × 2.5 Hz; one 4-H), 3.65 (ddd; J = 9.8, 6.5, and 2.7 Hz; 6a-H), 7.24 (tt; 2 × 7.2 and 2 × 1.6 Hz; *p*-phenyl-H), 7.31 (t; 2 × 7.2 Hz; 2 *m*-phenyl-H), 7.36 (dd; J = 7.2 and 1.6 Hz; 2 *o*-phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = 23.9, 25.6, 26.5, 26.8, 27.0, 27.4, and 28.0 (7 CH_2), 29.3 (C-4), 31.0 (CH_2), 33.3 (CH_2), 42.8 and 44.6 (C-12a, -12b), 80.1 (C-6a), 113.7 (C-4a), 127.6 (*p*-phenyl-C), 127.8 (2 *m*-phenyl-C), 129.0 (2 *o*-phenyl-C), 137.0 (*ipso*-phenyl-C), 146.5 (C-5).

Phenyl{(1*R,2*S**,7*S**,8*R**)-tricyclo[6.6.0.0^{2,7}]tetradec-2-yl}-methanone (23):** ^{1}H NMR ($CDCl_3$): δ = 1.03 (m; $J_{8,9\alpha}$ = 10.0 Hz; 9α-H), 1.03 (m; $J_{3\beta,4\alpha}$ = 13.5 Hz; 4α-H), 1.1−1.8 (m; 10 H), 1.50 (m; $J_{3\beta,4\beta}$ = 3.5 Hz; 4β-H), 1.52 and 1.64 (2 m; 6-CH_2), 1.70 (m; $J_{1,14\alpha}$ = 5.7 Hz; 14α-H), 1.77 (m; $J_{8,9\beta}$ = 3.5 Hz; 9β-H), 1.80 (m; $J_{1,14\beta}$ = 10.0 Hz; 14β-H), 1.83 (ddd; J = 14.2, 13.5, and 3.5 Hz; 3β-H), 1.91 (tdd; J = 2 × 10.0, 9.0, and 3.5 Hz; 8-H), 2.02 (dtd; J = 14.2, 2 × 3.6, and 1 Hz; 3α-H), 2.13 (ddd; J = 10.0, 9.0, and 5.7 Hz; 1-H), 2.19 (dddd; J = 10.0, 5.7, 2, and 1 Hz; 7-H), 7.38 (t; J = 2 × 7.2 Hz; 2 *m*-phenyl-H), 7.45 (t; J = 2 × 7.2 Hz; *p*-phenyl-H), 7.71 (d; J = 7.2 Hz; 2 *o*-phenyl-H). − ^{1}H,^{1}H NOE enhancements ($CDCl_3$): *o*-phenyl-H/1-H, *o*-phenyl-H/3α-H, *o*-phenyl-H/4α-H, *o*-phenyl-H/7-H, *o*-phenyl-H/both 14-H, 1-H/9α-H, 3α-H/14α-H, 7-H/9α-H. − ^{13}C NMR ($CDCl_3$): δ = 21.6 (C-4), 22.2 (CH_2), 23.6 (C-6), 24.6 (CH_2), 26.0 (CH_2), 26.9 (C-3), 27.1 (CH_2), 28.3 (CH_2), 28.4 (C-14), 35.7 (C-9), 38.0 (C-8), 40.2 (C-7), 47.5 (C-1), 53.0 (C-2), 128.1 (2 *m*- phenyl-C), 128.3 (2 *o*-phenyl-C), 131.5 (*p*-phenyl-C), 136.9 (*ipso*-phenyl-C), 207.2 (C=O).

Spiro[1,2,3,4,4a,9a-hexahydro-9*H*-fluorene-9,10′-9′-oxabicyclo-[6.2.0]decane] (Major Oxetane Photoproduct from 6): ^{1}H NMR ($CDCl_3$): δ = 1.0−1.7 (m; 15 H), 1.73 (dddd; J = 12.9, 12.0, 10.8, and 3.4 Hz; one 7′-H), 1.83 (m; 9a-H and 2 H), 1.91 (m; 1 H), 2.03 (ddt; J = 12.9, 5.5, and 2 × 3.5 Hz; one 7′-H), 3.04 (bt; 2 × 6 Hz; 4a-H), 3.18 (ddd; J = 11.5, 8.2, and 3.6 Hz; 1′-H), 4.83 (ddd; J = 10.8, 8.2, and 3.5 Hz; 8′-H), 7.10 (m; 1 H), 7.22 (m; 2 H), 7.63 (m; 1 H). − ^{13}C NMR ($CDCl_3$): δ = 25.6, 26.5, 27.7, 27.8, 28.2, 28.3, 28.6, 29.8, and 31.0, (9 CH_2), 38.1 (C−7′), 41.5 (C-9a), 48.6 (C-4a, -1′), 83.5 (C-8′), 99.5 (C-9), 122.7, 125.8, 126.0, 128.0 (C-5 through C-8), 143.9 and 147.3 (C-4b, -8a).

(4a*S,9a*R**)-9a-Cyclooctyl-1,2,3,4,4a,9a-hexahydrofluorenone (25):** M.p. 80 °C. − MS (EI): m/z = 296 [M^+]. − ^{1}H NMR ($CDCl_3$): δ = 1.02 (m; 2 H), 1.22 (dtd; J = 13.5, 2 × 9.0, and 3.5 Hz; one 8′-H), 1.27 (ddt; J = 13.5, 7.5, and 2 × 3.5 Hz; one 8′-H), 1.3−1.6 (m; 11 H), 1.33 (m; one 2′-H), 1.67 (m; 3 H; one 1-, one 2′-, and 1 H), 1.76 (ddd; J = 13.8, 10.4, and 4.5 Hz; one 1-H), 1.83 (dq; J = 13.9 and 3 × 4.5 Hz; one 4-H), 1.89 (ddt; J = 9.0, 8.0, and 2 × 3.5 Hz; 1′-H), 1.95 (ddt; J = 13.9, 11.5, and 2 × 5.3 Hz; one 4-H), 3.26 (dd; J = 5.3 and 4.5 Hz; 4a-H), 7.32 (t; J = 2 × 7.4 Hz; 7-H), 7.43 (d; J = 7.7 Hz; 5-H), 7.55 (t; J = 2 × 7.5 Hz; 6-H), 7.69 (d; J = 7.7 Hz; 8-H). − ^{1}H,^{1}H NOE enhancements: 4a-H/5-H, 4a-H/1′-H, 4a-H/2′-H at δ = 1.67, 4a-H/8′-H at δ = 1.22. − ^{13}C NMR ($CDCl_3$): δ = 17.9, 18.9, 26.1, and 26.2 (4 CH_2), 26.3 (C-4), 26.6, 26.9, 27.3 (3 CH_2), 27.8 (C-1), 29.0 (C-2′), 29.5 (C-8′), 41.3 (C-4a), 43.3 (C-1′), 57.5 (C-9a), 123.3 (C-8), 124.9 (C-5), 127.2 (C-7), 134.4 (C-6), 137.7 (C-4b), 158.1 (C-8a), 212.8 (C-9).

Spiro[1,2,3,4,4a,9a-hexahydro-9*H*-fluorene-9,10′-9′-oxabicyclo-[6.2.0]decane] (Minor Oxetane Photoproduct from 6): ^{1}H NMR ($CDCl_3$): δ = 0.9−1.4 (m; 7 H), 1.46 (m; 1 H), 1.60−1.95 (m; 10 H), 2.06 (dq; J = 14.0 and 3 × 4.0 Hz; one 4-H), 2.11 (ddd; J = 12.8, 5.2, and 3.4 Hz; one 7′-H), 2.75 (ddd; J = 12.1, 7.8, and

2.9 Hz; 1′-H), 2.85 (dt; J = 10.6 and 2 × 5.9 Hz; 9a-H), 3.04 (dddt; J = 5.9, 5.7, 4.0, and 2 × 1.0 Hz; 4a-H), 4.54 (td; J = 2 × 7.8 and 3.4 Hz; 8′-H), 7.13 (m; 5-H), 7.25 (m; 6-H and 7-H), 7.55 (quasi-d; 8-H). − ^{13}C NMR ($CDCl_3$): δ = 21.9, 23.4, 24.5, 26.4 (4 CH_2), 26.5 (C-4), 28.2, 28.3, 28.7, and 29.7 (4 CH_2), 38.1 (C-7′), 40.8 (C-4a), 43.6 (C-9a), 54.0 (C-1′), 83.4 (C-8′), 94.0 (C-9), 122.6 (C-5), 124.2 (C-8), 126.7 and 128.1 (C-6, −7), 143.8 and 147.9 (C-4b, -8a).

8,9-Benzotetracyclo[9.6.0.0^{2,7}.0^{2,10}]heptadecan-10-ol (Secondary Photocyclisation Product from 25): ^{1}H NMR ($CDCl_3$): δ = 1.07 (m; 1 H), 1.15−1.95 (m; 20 H), 2.00 (ddd; J = 10, 9, and 2.5 Hz; 11-H), 2.06 (ddd; J = 11, 9, and 2.5 Hz; 1-H), 3.25 (t; 2 × 6.3 Hz; 7-H), 7.20 (m; 2 H), 7.23 (m; 2 H). − ^{1}H,^{1}H-NOE enhancement: 1-H/7-H. − ^{13}C NMR ($CDCl_3$): δ = 19.6, 20.0, 26.3, 27.3, 27.5, 28.0, 28.0, 28.3, 28.5, and 30.6 (10 CH_2) 42.3 (C-7), 47.4 (C-11), 49.3 (C-1), 53.3 (C-2), 85.4 (C-10), 122.0, 123.5, 126.9, 127.6 (4 CH), 147.5 and 148.3 (C-8, −9).

(4a*S,9a*R**)-9a-(1′*R**,2′*R**- and 1′*S**,2′*S**-2′-Deuteriocyclooctyl)-1,2,3,4,4a,9a-hexahydro-5,6,7,8-tetradeuteriofluoren-9-one (25-d$_5$):** The ca. 1:1 mixture of the two 2′-deuterio compounds **25-d$_5$** was prepared by irradiation of the pentadeuteriophenylmethanone **1-d$_5$** and (*E*)-cyclooctene as described above for nondeuterated **25**. The NMR spectra (500 MHz ^{1}H and 125 MHz ^{13}C) showed the following differences relative to nondeuterated **25**: (*i*) The four aromatic C−H moieties were replaced by C−D according to both the ^{1}H and ^{13}C BB spectra. (*ii*) The 1′-H signal at δ = 1.89 was changed from a ddt (J = 9.0, 8.0, and 2 × 3.5 Hz) to a clean ddd (J = 9.0, 8.0, and 3.5 Hz), indicating that the fifth D atom was in a vicinal position. Since the two larger couplings (J = 9.0 and 8.0 Hz) correspond to antiperiplanar H,H arrangements and the two smaller ones (J = 2 × 3.5 Hz) to synclinal H,H arrangements, the cyclooctane 1′-H is *seq-trans*-configured relative to each of the two H atoms coupled to it by the larger coupling constants. This and the disappearance of exactly one 3.5 Hz coupling means that the exocyclic C−C bond on the cyclooctane and the vicinal D atom are also *seq-trans*-configured to each other. This demonstrates a clean suprafacial addition of D and fluorenonyl to (*E*)-cyclooctene, irrespective of the distribution of the D atom between C-2′ and C-8′. (Note that after the D atom has been placed on C-8′, the cyclooctyl ring positions have to be renumbered so as to change C-8′ into -2′, whereas no renumbering is carried out if the D atom has been placed on C-2′.) Further differences in the NMR spectra show that this distribution is ca. 1:1, with the D atom replacing 2′-H (signal at δ = 1.67) and 8′-H (signal at δ = 1.27). (*iii*) In the ^{13}C BB spectra, about half of the C-8′ singlet at δ = 29.5 is replaced by a small triplet (J = 18.5 Hz) at δ = 29.1; similarly, about half of the C-2′ singlet at δ = 29.0 is replaced by a small triplet (J = 19.1 Hz) at δ = 28.6. (*iv*) The proton integrals in the ranges δ = 1.15−1.60 and 1.60−1.80 are reduced by approximately one half H atom each. (*v*) The 8′-H signal at δ = 1.27 is reduced in intensity but unchanged in shape; the 8′-H signal at δ = 1.22 is unchanged in intensity but changed in shape.

Analytical Irradiation of 1 in the Presence of (*E*)-Cyclooctene: Six equal Solidex glass tubes, each containing 13.1-ml samples of 250 mg of **1** (0.1 M) and varying concentrations of (*E*)-cyclooctene (0.5 M, 1.0 M, 1.94 M; 2 samples of each) in acetonitrile, were placed in a merry-go-round apparatus with a central 125-W high pressure mercury lamp (Philips HPK 125) and irradiated for 4 h, after which time about half of **1** had been converted into products. [Concentrations of (*E*)-cyclooctene higher than the ones above resulted in inhomogeneous solutions and were discarded.] A 1-ml aliquot from each sample was concentrated at room temp. and 0.1 mbar, which did not remove all of the (*E*)-cyclooctene, and the residue was analysed by 400-MHz ^{1}H NMR spectroscopy in the regions δ = 2.5−5 and 7−8, making use of the known absorption of the individual components. For the results see Table 1.

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[1] Unbracketed compounds in Scheme 1 were stable enough to be isolated or detected in solution even after prolonged times at room temperature. In all schemes in this work, arrows bearing "*hν*" refer to photochemical reactions, while arrows without "*hν*" refer to dark reactions at room temperature. In all schemes, stereoformulae are intended to designate relative, not absolute, configurations.
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