Photochemistry of Arylidene-β-ionones: A Highly Efficient Route to Novel Tricyclic Ketones through Intramolecular, Exoselective Photochemical (4 + 2) Cycloadditions, Occurring Only in an Aqueous−Organic Solvent

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(*E,E*)-Arylidene-β-ionones (**1a**−**f**) are converted to 1,7,7-trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo-[4.4.0]deca-3,5-dienes (**3a**−**f**, ~90%) by irradiating in anhydrous solvents. Irradiation of (**3a**−**f**) in aqueous methanol results in *Z,E*-arylidene-β-ionones (**2**), through retro-electrocyclization, which undergoes an intramolecular, *exo*-selective [4 + 2] photocycloaddition leading to 11-(*exo*)-aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-ene-3-ones (**8a**−**f**, 60−80%). The latter rearrange over silica gel to afford, quantitatively, 5-aryl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-ones (**5a**−**f**). Irradiation of **1a**−**f** in aqueous methanol leads to **8a**−**f**, except in case of **1c,f** wherein formation, respectively, of tricyclic ketones **9c** (55%) and **9f** (80%), derived from photodeconjugation in **2**, followed by intramolecular [4 + 2] cycloaddition, is observed.

Introduction

It has been reported that (*E,E*)-arylidene-β-ionones (**1a**−**f**) when irradiated under anhydrous conditions undergo regioselective *E*−*Z* isomerization, which is followed by 6π-electrocyclization, yielding 1,7,7-trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]-deca-3,5-dienes (**3a**−**f**) in high yields.[1] Further it has been reported by Gandhi et al.[2] that **3a**−**c**, on irradiation in aqueous solvents such as methanol, acetonitrile, and acetone, undergo an intramolecular phototransformation to yield 11-(*endo*)-aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**4a**−**c**) in high yield; the latter phototransformation is postulated to involve an intramolecular photochemical ($\pi_a4 + \pi_s2$) cycloaddition in *Z,E*-arylidene-β-ionone (**2**, Scheme 1). In view of the diverse modes of phototransformation available to conjugated ketones[3] and β-ionone derivatives,[4] and also the known lability of bicyclic systems such as **4** (both under UV irradiations[5] and under acidic conditions[6]), we have recently reinvestigated the above phototransformation.[7]

Initially, compounds **1a**−**c** were irradiated in anhydrous benzene, under nitrogen atmosphere, to obtain the corresponding pyrans **3a**−**c**, which were isolated and identified spectroscopically.[1] Further irradiation of pyrans **3a**−**c** was carried out in aqueous methanol under conditions as employed by Gandhi et al.,[2] whereupon column chromatographic resolution of the photolyzates led to isolation of substances that gave the same melting points, as well as NMR and other spectroscopic data as reported for **4a**−**c**.[2] However, X-ray crystallographic structure determination of the compound derived from **3b** (earlier assigned as **4b**) led to its actual structure as 7,11,11-trimethyl-5-p-tolyl-tricyclo-[5.4.0.0^{3,6}]undec-1-ene-4-one (**5b**).[8] Since the spectroscopic data earlier attributed to **4a,c** can be successfully explained by structure **5a,c**, hence it is logical that structures of **4a,c** shall also revised to **5a,c**, respectively.

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(1) Gandhi, R. P.; Kumar, S.; Aryan, R. C.; Ishar, M. P. S. *Synth. Commun.* **1989**, *19*, 1759.

(2) (a) Gandhi, R. P.; Aryan, R. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1024. (b) Aryan, R. C. Ph.D. Thesis, Submitted to Indian Institute of Technology, Delhi, New Delhi, 1985 (IIT-Delhi Library Acc. No. 1292).

(3) (a) Baldwin, S. W.; Gross, P. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcell Dekker: New York, 1981; Vol. 5, Chapter 2, p 162. (b) Elad, O. In *Organic Photochemistry*; Marcell Dekker: New York, 1983; Vol. 2, Chapter 2, p 109. (c) Trecker, D. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcell Dekker: New York, 1983; Vol. 2, Chapter 5.

(4) (a) Frei, B.; Eichenberger, H.; Wartburg, B.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1977**, *60*, 2968. (b) Ishii, K.; Lyle, T. A.; Schweizer, B.; Frei, B. *Helv. Chim. Acta* **1982**, *65*, 595 and references therein. (c) Ishii, K.; Mathies, P.; Nishio, T.; Wolf, H. R.; Frei, B.; Jeger, O. *Helv. Chim. Acta* **1984**, *67*, 1175. (d) van Wageningen, A.; Cerfontain, H.; Greenevasen, A. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1283. (e) van Wageningen, A.; Cerfontain, H. *Tetrahedron Lett.* **1972**, 3679. (f) Cerfontain, H.; Geenevasen, J. A. J. *Tetrahedron* **1981**, *37*, 1571.

(5) (a) Erman, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 3828. (b) Erman, W. F.; Kretschmar, H. C. *J. Am. Chem.* Soc. **1967**, *89*, 3842 and references therein.

(6) (a) Erman, W. F.; Treptow, R. S.; Bakuzis, P.; Wenkert, E. *J. Am. Chem.* Soc. **1971**, *93*, 657.

(7) Doubts regarding the assigned structure were also raised by the recorded observation[2b] that the compounds assigned as **4a**−**c** did not rearrange under acidic conditions, which was in sharp contrast to reported[6] facile rearrangement of related systems under acidic conditions.

(8) The X-ray structure plot of **5b** (Figure 1) refers to data of crystal system monoclinic; space group $P2_1/c$; unit cell dimensions a = 11.0125(4) Å, b = 14.2946(4) Å, c = 11.8980(4) Å, $\alpha = \gamma = 90°$, β = 110.8180(10)°; V = 1750.70(10) Å^3; Z = 4; calculated density = 1.117 Mg/m^3; final R indices [$I > 2\sigma(I)$] R1 = 0.0568, wR2 = 0.1414; R indices (all data) R1 = 0.1224, wR2 = 0.1753; goodness-of-fit on F^2 = 0.825.

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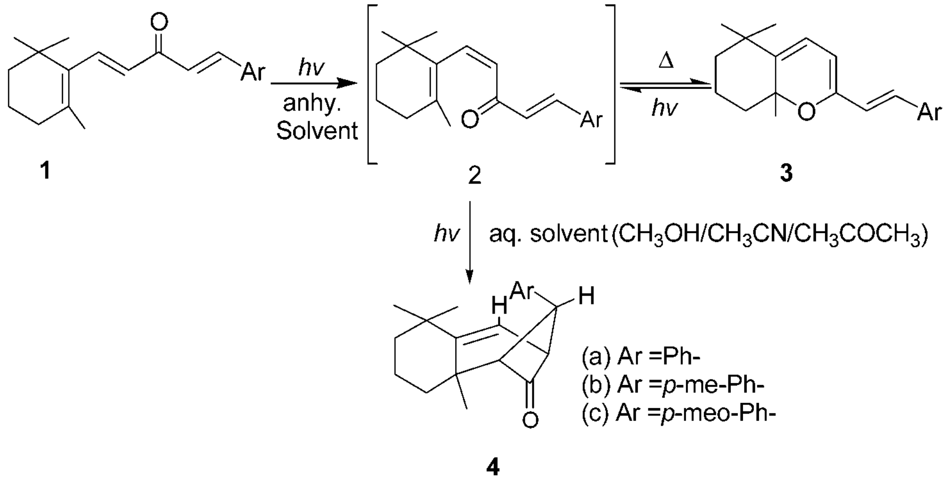
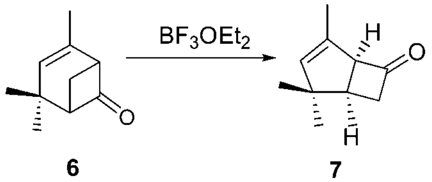
Scheme 1

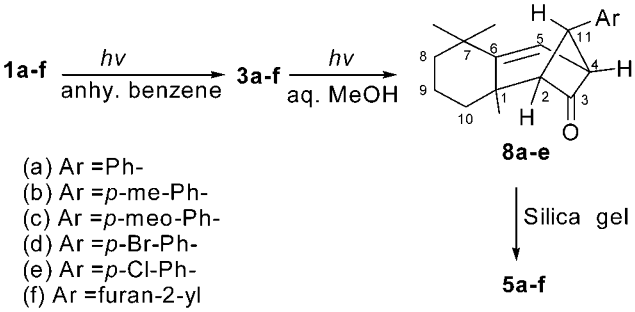


It has been reported[6] in the literature that cyclobutanones related to **5a**−**c**, e.g., 2,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**7**), are easily derived from highly labile 2,4,4-trimethylbicyclo[3.1.1]hept-2-en-6-one (**6**) under both acidic and basic conditions (Scheme 2).

Scheme 2



Scheme 3



The next step, therefore, was to establish whether compounds **5a**−**c** are generated directly during irradiation of **3a**−**c**, respectively, or are derived from rearrangement of an initially formed photoproduct. Toward this end compound **3b** was irradiated in aqueous methanol under the same conditions as employed earlier, and the ^{1}H NMR spectrum of the crude residue, obtained on concentration of photolyzate under vacuum, was recorded. To our great surprise the ^{1}H NMR spectrum clearly indicated that not even a trace of **5b** was present. Similar absence of **5a**,**c** in the crude photolyzates obtained, respectively, from **3a**,**c** was, subsequently, established by the ^{1}H NMR spectral monitoring. These ^{1}H NMR spectra also indicated that identical types of photoproducts are initially produced in all the cases. However, when these photolyzates were passed through a silica gel column or their chloroform solutions were stirred with silica gel for 3 h, the photoproducts were quantitatively converted to corresponding **5**.[9] These experiments clearly established that **5a**−**c** are not produced directly on irradiation but rather are derived from rearrangement of an initially formed photoproduct on silica gel. However, it was not possible to isolate the initially formed photoproduct in requisite pure form for its characterization as it resisted attempts at crystallization from the photolyzate and during attempted chromatographic purification it was quantitatively converted to corresponding **5**.

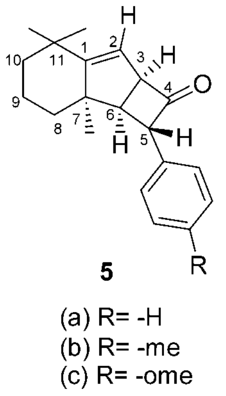


Figure 1.

Taking cognizance of the similarity between the NMR spectral features of the elusive initially formed photoproduct and the NMR spectral data reported for 11-(*exo*)-*p*-bromophenyl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**8d**)[10] (Scheme 3), the investigations were subsequently extended to (**1d,e**). The arylidene-β-ionones (**1d,e**) were converted to the corresponding pyrans (**3d,e**) by irradiating their anhydrous benzene solutions under nitrogen atmosphere; the latter were isolated by column chromatography and identified spectroscopically. When **3d,e** were irradiated in aqueous methanol, and after completion of reaction (TLC, 3.5 h) the photolyzates were concentrated under vacuum and ^{1}H NMR spectra of the crude products were recorded, they revealed the forma-

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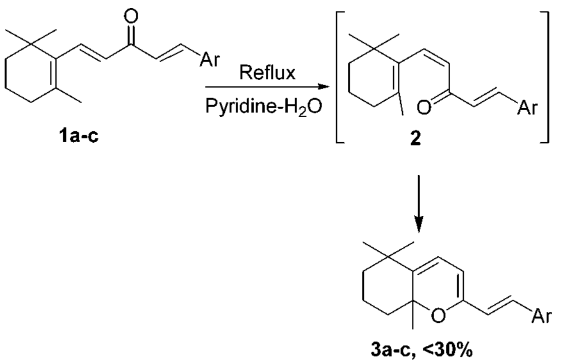
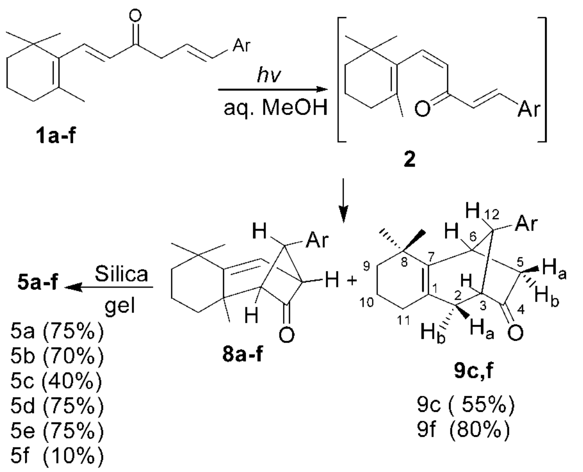
(9) The crude photolysates were >80% pure as indicated by TLC and ^{1}H NMR; however, the major product was indistinguishable from **5a**−**c** on TLC.

(10) It has been reported[2b] that irradiation of pyrans **3a**−**c** under aqueous conditions leads to the *endo* products (**4a**−**c**), whereas irradiation of **3d** affords (after chromatographic resolution) the corresponding *exo* product (**8d**). This differing behavior has been attributed to a change in the nature of involved frontier interaction in the photocycloaddition step!

Scheme 4



Scheme 5



tion of photoproducts having critical NMR spectral features similar to those displayed by photoproducts derived from **3a**−**c**. However, in the case of **3d,e** the photoproducts (**8d,e**) crystallized out of the crude photolyzates. These were recrystallized from hexane, and complete spectroscopic data were recorded. A comparison of the spectral data with the related systems[5,6,11] led to characterization of these compounds as 11-(*exo*)-aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**8d,e**), thus confirming the earlier assignment of **8d**.[2a,10] Here the presence of a singlet in the ^{1}H NMR spectrum at δ 3.09 assigned to C$_{11}$-H(*endo*) was critical, i.e., lack of its observable coupling with C$_2$-H and C$_4$-H led to the assigned stereochemistry at C$_{11}$. However, **8d,e** on stirring with silica gel or passing through a silica gel column underwent facile rearrangement to corresponding 5-aryl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-ones (**5d,e**), which contradicts the reported[2b] isolation of **8d** after column chromatography over silica gel. The investigations were also extended to **3f**, and the results so far have established that irradiation of **3a**−**f** in aqueous solvent produces only the 11-(*exo*)-aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**8a**−**f**) and that the latter undergo facile rearrangement in the presence of silica gel to the corresponding 7,11,11-trimethyl-5-aryltricyclo[5.4.0.0^{3,6}]undec-1-ene-4-ones (**5a**−**f**, Scheme 3).

Verification of the formation of tricyclic ketones **8a**−**e** as a photochemical transformation has been established by refluxing the (*E,E*)-arylidene-β-ionones (**1a**−**c**) in aqueous pyridine,[12] wherein their isomerization to (*Z,E*)-arylidene-β-ionones is accompanied with electrocyclization to pyrans **3a**−**c** (Scheme 4). Although the yield of **3a**−**c** under thermal conditions is low (<30%) and a complex mixture is obtained, cycloaddition leading to formation of **8a**−**c** (hence **5a**−**c**) is not observed.

Direct irradiation of (*E,E*)-arylidene-β-ionones **1a**−**f** in MeOH−H$_2$O, under nitrogen atmosphere, was taken up next because it has been reported[2b] that it gives similar products as are obtained on irradiation of corresponding pyrans,[13] though with slightly reduced yields. A ^{1}H NMR examination of the crude photolyzates obtained on irradiation of **1a**−**f** in aqueous methanol revealed the formation of only the corresponding [4 + 2] adducts (**8a,b,d,e**) in the case of photolyzates of (**1a,b,d,e**); however, in the case of **1c,f** the ^{1}H NMR of photolyzates indicated the formation of another product in each case, besides **8c** and **8f**, respectively. Consequently, the photolyzates derived from **1c,f** were resolved column chromatographically to obtain **5c,f** and the other products, which have been characterized as **9c** and **9f**, respectively (Scheme 5).

The structures of **9c,f** have been established by rigorous spectroscopic analysis including 2D NMR (^{1}H COSY and Het COSY) and DEPT ^{13}C NMR spectral measurements. The initial inference regarding involvement of a methyl group in phototransformation (**1c**,**f** → **9c**,**f**) was based on NMR spectra that indicated the presence of only two methyl groups. Complete ^{1}H NMR assignments were aided by known, rigorously worked out ^{1}H NMR couplings in the case of closely related bicyclo[3.2.1]oct-2-ene systems.[14] Here again the lack of ^{1}H coupling between C$_{12}$-H and C$_3$-H/C$_6$-H, the presence of long-range coupling between C$_{12}$-H and C$_5$-H$_b$ (due to W relationship, observed by ^{1}H COSY), coupling involving C$_3$-H and C$_6$-H (due to W relationship, observed by ^{1}H COSY), and a coupling pattern involving C$_6$-H with C$_5$-H's as also C$_3$-H with C$_2$-H's were quite instructive.[13] The structural conclusions are also corroborated by ^{13}C NMR spectral assignments.

Mechanistically, the conversion of **3a**−**f** to **8a**−**f** involves a photochemical, *exo*-selective ($\pi_s^4 + \pi_a^2$, Scheme 6) addition in (*Z,E*)-arylidene-β-ionone (**2**); the latter is derived from photochemical retro-electrocyclization of **3a**−**f**.[12,15] Since this intramolecular cycloaddition occurs only in aqueous solvent and is not realized in solvents such as dry CH$_3$CN,[2] the role of water may have to be identical with the generally observed role of aqueous medium in facilitating [4 + 2] cycloadditions,[16] though a possible involvement of intramolecular electron transfer and intermediates such as **A** and **B** may be the other plausible alternative (Scheme 6). Involvement of intermediates such as **B** has been postulated in photoreorganization of verbenone to bicyclic ketones related to **8**.[5]

The mechanism of rearrangement of bicyclic-ketones related to **8** to cyclbutanones of type **5**, including stereo-

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(11) (a) Kaplan, F.; Schulz, C. O.; Weisleder, D.; Klopfenstein, C. *J. Org. Chem.* **1968**, *33*, 1728. (b) Bates, R. B.; Thalacker, V. P. *J. Org. Chem.* **1968**, *33*, 1730.

(12) Marvell, E, N.; Chadwick, T.; Caple, G.; Gosink, T.; Zimmer, G. *J. Org. Chem.* **1972**, *37*, 2992.

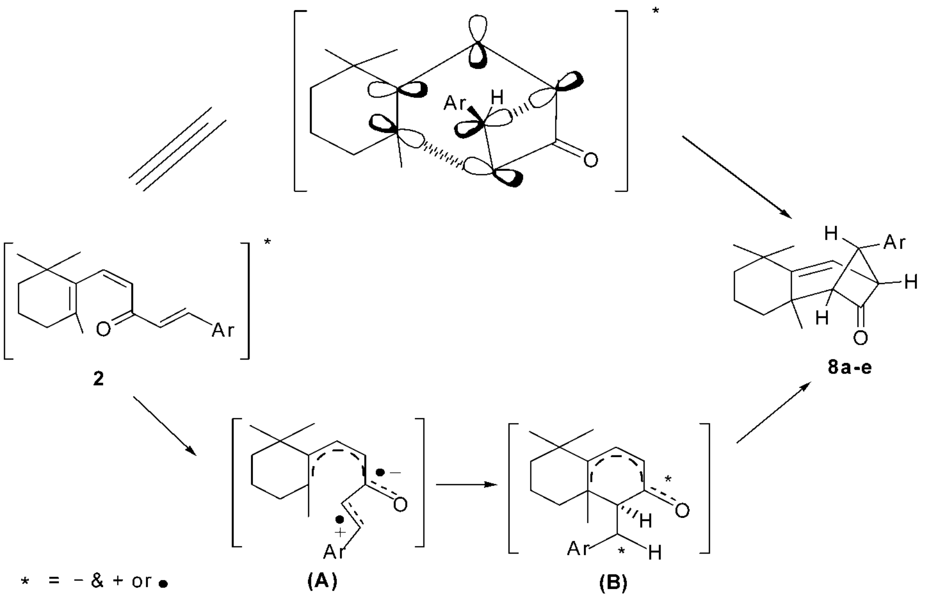
(13) Direct irradiation of only **1a**−**d** in aqueous methanol has been described. [2b]

(14) (a) Jefford, C. W.; Mahajan, S.; Waslyn, J.; Waegell, B. *J. Am. Chem. Soc.* **1965**, *87*, 2183. (b) Waegell, B.; Jefford, C. W. *Bull. Soc. Chim. France* **1964**, 844. (c) Jefford, C. W.; Waegell, B.; Ramey, K. *J. Am. Chem. Soc.* **1965**, *87*, 2191.

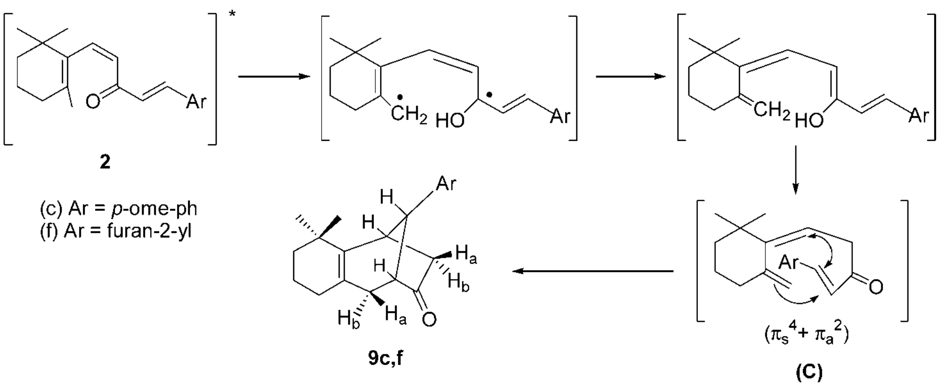
(15) Marvell, E, N.; Caple, G.; Gosink, T. A.; Zimmer, G. *J. Am. Chem. Soc.* **1966**, *88*, 619.

(16) Kumar, A. *Chem. Rev.* **2001**, 101, 1 and references therein.

Scheme 6



Scheme 7



chemical disposition around cyclobutanone ring, has been well investigated and has been reported to proceed under a variety of conditions including acid catalysis.[6] The important aspect that requires mentioning here is that conversion of **8** to **5** on silica gel is quantitative and stirring of **8b,e** with pTSA (catalytic amount) in chloroform led to **5b,e** along with a mixture of other products (Tlc, ^{1}H NMR); no attempt was made to isolate the products, though formation of a number of them is anticipated.[6]

Formation of **9c,f** from **1c,f**, quite apparently, involves a photochemical H-abstraction in **2**, by the carbonyl oxygen leading to deconjugated intermediate (**C**), which is followed by an intramolecular *exo*-selective [4 + 2] cycloaddition; such intramolecular H-abstraction and deconjugation are precedented in β-ionone photochemistry.[4]

However, two interesting observations of the present investigations are the role of aqueous solvent in promoting the H-abstraction and cycloaddition, and the role of the nature of the aryl group. In the case of irradiation of **3c** in aqueous methanol, no detectable amount of **9c** is produced and only **8c** (and hence **5c**) is produced in 70% yield, whereas direct irradiation of **1c** generates **9c** to the extent of 55%. On the other hand, direct irradiation of **1f** in aqueous methanol produces **9f** to the extent of 80% and **8f** is also produced (~40%) during irradiation of **3f** in aqueous methanol.[17] This influence of relatively electron-rich aryl groups (*p*-methoxyphenyl and furan-2-yl) is not in keeping with the known involvement of n–π* photoexcited state of carbonyl group in H-abstraction and suppression of H-abstraction when the carbonyl group is extensively conjugated, particularly with electron-rich π-systems; in the latter case the π–π* triplet is reported to be lower than the n–π* triplet.[18]

Conclusions

Though the mechanistic aspects including the role of aqueous solvents[19] as well as possible involvement of intramolecular electron transfer/exciplexes in the observed phototransformations require further probing, the present investigations have led to correction of structural

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[17] Compound **9f** was missed during initial irradiation of **3f** in aqueous methanol as a result of close R_f of **9f** and **8f** and probably the relative instability of **5f**, **8f**, and **9f**. However after isolation and characterization of **9f** from direct irradiation of **1f** in aqueous methanol, a reinspection of the ^{1}H NMR spectrum of crude obtained from the irradiation of **3f** in aqueous methanol revealed that **8f** and **9f** were formed approximately in the ratio of 60:40.

[18] (a) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329. (b) Wagner, P. J.; Kemppainen, A. E.; Scott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604. (c) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

[19] During present investigations it has been observed that ~2% of H_2O is the optimum amount; increasing the amount of water beyond 2% leads to formation of multiple products.

assignments, establishment of *exo*-selectivity of these photocycloadditions, and discovery of an alternative mode of phototransformation of arylidene-β-ionones, i.e., formation of **9c,f**. These high throughput phototransformations, which involve rather uncommon intramolecular, stereoselective [4 + 2] cycloadditions,[20] have provided easy access to tricyclic cyclobutanones and complex molecular frameworks. Many such cyclobutanones have proven to be extremely versatile synthons involved in the total synthesis of a number of important biologically active molecules.[21]

Experimental Section

General. Starting materials and reagents were purchased from commercial suppliers and used after further purification (crystallization/distillation). Arylidene-β-ionones were prepared by condensing the corresponding aldehydes with β-ionone (Fluka) in the presence of sodium hydroxide in a mixture of water and ethyl alcohol.[1,2] NMR chemical shifts are reported in ppm as downfield displacements from tetramethylsilane used as the internal standard, and *J* values are in Hertz. All melting points, measured in open glass capillary, are uncorrected.

General Procedure for Irradiation of Arylidene-β-ionones (1a−f) in Benzene. Arylidene-β-ionones **1a−f** (500 mg) were dissolved in anhydrous benzene and taken in an immersion well type Pyrex glass, water-cooled photoreactor, and the solutions were purged with dry oxygen-free N_2 for at least 15 min prior to irradiation. The irradiation was carried out for 0.5 h with a 125-W medium pressure Hg arc placed coaxially inside the reactor, and N_2 was continuously bubbled during irradiation. At the end of reaction (TLC), solvent was removed from photolyzates under reduced pressure using an Eyela rotary evaporator, and products were separated by column chromatography over silica gel (Acme Synthetic Chemicals, Mumbai, India, 60−120 mesh, 20 g, packed in hexane), using hexane as eluant, to obtain **3a−f**. Identity of the products was established by spectroscopic analysis.[2]

General Procedure for Irradiation of 1,7,7-Trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]deca-3,5-dienes (3a−f) in Aqueous Methanol. 1,7,7-Trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]deca-3,5-dienes (**3a−f**, 400 mg)were dissolved in a mixture of methanol (250 mL) and water (5 mL) and taken in an immersion well type Pyrex glass, water-cooled photoreactor, and the solutions were purged with dry oxygen-free N_2 for at least 15 min prior to irradiation. The irradiation was carried out for 3.5 h with a 125-W medium pressure Hg arc placed coaxially inside the reactor, and N_2 was continuously bubbled during irradiation. Progress of the reaction was monitored by TLC. At the end of reaction solvent was distilled off from photolyzates under reduced pressure using an Eyela rotary evaporator. Products were extracted with hexane, and separation by column chromatography over silica gel (Acme Synthetic Chemicals, Mumbai, India, 60−120 mesh, 15 g, columns packed in hexane) using hexane−chloroform as eluant, yielded 5-aryl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-ones (**5a−f**), whose physical and spectroscopic data are as follows.

5-Phenyl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-one (5a). Colorless solid, yield 80%, mp 75−76 °C (hexane). IR (KBr)/cm^{-1}: 1770(C=O), 1600(m), 1500(m), 1460(m), 1380(w−m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.28−7.23(m, 5H, arom.-Hs), 5.43(br d, 1H, $J = 3.0$ Hz, C_2−H), 4.4(dd, 1H, $J_{5,6} = 6.8$, $J_{5,3} = 3.3$ Hz, C_5−H), 4.03−3.98(m, 1H, C_3−H), 2.65(t, 1H, $J \sim 6.8$ Hz, C_6−H), 1.84−1.46(m, 6H, 3 × $-CH_2$), 1.31(s, 3H, $-CH_3$), 1.18(s, 3H, $-CH_3$), 1.17(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 201.3(C=O), 158.8(C_1), 136.5(q. arom.), 128.1(q. arom.), 126.9(CH), 126.22(CH), 117.8(C_2), 66.4(C_5), 62.1(C_3), 49.2(C_{11}), 48.4(C_6), 40.3(C_{10}), 34.5(C_7), 32.9(C_8), 31.4($-CH_3$), 29.7($-CH_3$), 28.5($-CH_3$), 18.8(C_9). MS: *m*/*z* 281($M^+ + 1$, 7), 280(M^+, 22), 238(98), 182(42), 168(50), 163(97), 162(28), 154(75), 148(96), 132(30), 130(20), 129(20), 120(20). Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.61; H, 8.68.

5-*p*-Tolyl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-one (5b). Colorless solid, yield 78%, mp 60−61 °C (hexane). IR (KBr)/cm^{-1}: 1766.7(C=O), 1595(m), 1517.9(m), 1458(m), 1440(w), 1371(m), 1357.8(m), 1170(w), 1084(m), 1005(w), 980(w), 831(m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.11(s, 4H, arom.-Hs), 5.44(br d, 1H, $J = 2.1$ Hz, C_2-H), 4.45(dd, 1H, $J_{5,6} = 6.8$, $J_{3,5} = 3.0$ Hz, C_5-H), 4.08−4.00(m, 1H, C_3-H), 2.68(dis t, 1H, $J \approx 6.8$ Hz, C_6-H), 2.32(s, methyl on aromatic ring), 1.88−1.48(m, 6H, 3 × $-CH_2$), 1.30(s, 3H, $-CH_3$), 1.18(s, 3H, $-CH_3$), 1.17(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 205.78(C=O), 159.59(C_1), 136.10(q. arom.), 133.63(q. arom.), 129.14(CH), 127.16(CH), 117.65(C_2), 66.82(C_5), 62.47(C_3), 49.68(C_{11}), 48.59(C_6), 40.48(C_{10}), 34.64(C_7), 32.84(C_8), 31.41($-CH_3$), 28.73($-CH_3$), 28.46($-CH_3$), 21.02(methyl on aromatic ring), 18.82(C_9). MS: *m*/*z* 295($M^+ + 1$, 6), 294(M^+, 26), 279(60), 266(40), 251(25), 162(49), 147(100), 132(87), 119(15), 91(18), 77(11). Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.62; H, 8.96.

5-*p*-Anisyl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-one (5c). Colorless solid, yield 70%, mp 96−97 °C (hexane). IR (KBr)/cm^{-1}: 1775(C=O), 1622(m), 1591(m), 1521(w−m), 1478(m), 1451(m), 1308(m), 1260(m−s), 1186(m), 853(m), 830(m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.10(d, 2H, $J = 8.6$ Hz, arom.-Hs), 6.81(d, 2H, $J = 8.6$ Hz, arom.-Hs), 5.43(br d, 1H, $J = 2.1$ Hz, C_2-H), 4.40(dd, 1H, $J_{5,6} = 6.8$, $J_{3,5} = 3.0$ Hz, C_5-H), 4.06−4.00(m, 1H, C_3-H), 3.77(s, 3H, $-OCH_3$), 2.62(t, 1H, $J \approx 6.3$ Hz, C_6-H), 1.87−1.47(m, 6H, 3 × $-CH_2$), 1.29(s, 3H, $-CH_3$), 1.17(s, 3H, $-CH_3$), 1.16(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 202.06(C=O), 158.09(C_1), 158.01(q. arom.), 128.41(CH), 117.86(C_2), 114.12(CH), 67.76(C_5), 62.23(C_3), 55.20($-OCH_3$), 49.84(C_{11}), 49.00(C_6), 40.64(C_{10}), 34.79(C_7), 33.02(C_8), 31.58($-CH_3$), 28.90($-CH_3$), 28.64($-CH_3$), 19.00(C_9). MS: *m*/*z* 311($M^+ + 1$), 310(M^+), 296(10), 295(45), 282(52), 268(19), 267(93), 211(17),148(100), 147(15), 121(90), 91(18), 71(8). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.19; H, 8.50.

5-*p*-Bromophenyl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-one (5d). Colorless solid, yield 80%, mp 84−85 °C (hexane). IR (KBr)/cm^{-1}: 1764(C=O), 1593.4(s), 1541(m), 1508(m), 1474(w), 1458(m), 1385(m), 1354(m), 1090(m), 853(m), 831(m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43(d, 2H, $J = 8.4$ Hz, arom.-Hs), 7.10(d, 2H, $J = 8.4$ Hz, aroma.-Hs,), 5.4(d, 1H, $J = 2.1$ Hz, C_2-H), 4.44(dd, 1H, $J_{5,6} = 6.9$, $J_{3,5} = 3.0$ Hz, C_5-H), 4.08−4.02(m, 1H, C_3-H), 2.65(t, 1H, $J = 6.3$ Hz, C_6-H), 1.76(m, 2H, $-CH_2$), 1.67−1.49(overlapping multiplets, 4H, 2 × $-CH_2$), 1.30(s, 3H, $-CH_3$), 1.18(s, 3H, $-CH_3$), 1.16(s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.22(C=O), 159.86(C_1), 135.66(q. arom.), 131.55(CH), 128.97(CH), 120.59(q. arom.), 117.43(C_2), 67.03(C_5), 61.99(C_3), 49.75(C_{11}), 48.41(C_6), 40.41(C_{10}), 34.65(C_7), 32.91(C_8), 31.37($-CH_3$), 28.65($-CH_3$), 28.44($-CH_3$), 18.80(C_9). MS: *m*/*z* 361($M^+ + 2$, 4), 360($M^+ + 1$, 15), 359(M^+, 12), 358(16), 345(21), 343(17), 333(20), 332(78), 331(22), 330(82), 318(42), 317(85), 316(45), 315(85), 284(30), 283(37), 277(32), 275(20), 263(32), 262(29), 261(54), 260(23), 259(30), 248(33), 247(49), 246(23), 245(50), 147(100). Anal. Calcd for $C_{20}H_{23}BrO$: C, 66.86; H, 6.45. Found: C, 66.79; H, 6.50.

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5-*p*-Chlorophenyl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]-undec-1-ene-4-one (5e). Colorless solid, yield 80%, mp 99−100 °C (hexane). IR (KBr)/cm^{-1}: 1767(C═O), 1593.4(s), 1509(m), 1491(w), 1458(m), 1385(m), 1354(m−s), 1088(w), 1071(w), 1015(w), 853(m), 831(m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28 (d, 2H, $J = 8.4$ Hz, arom.-Hs), 7.16 (d, 2H, $J = 8.4$ Hz, arom.-Hs), 5.43 (d, 1H, $J = 2.1$ Hz, C_2-H), 4.46 (dd, 1H, $J_{5,6} = 6.8$, $J_{3,5} = 3.0$ Hz, C_5-H), 4.09−4.05(m, 1H, C_3-H), 2.65 (t, 1H, $J \sim 6.3$ Hz, C_6-H), 1.86−1.79 (m, 2H, -CH_2), 1.67−1.49(m, 4H, 2 × -CH_2), 1.30 (s, 3H, -CH_3), 1.17 (s, 3H, -CH_3), 1.15 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.61(C═O), 159.96(C_1), 135.18-(q. arom.), 132.62(q. arom.), 128.68(CH), 117.52(C_2), 67.09(C_5), 62.02(C_3), 49.84(C_{11}), 48.54(C_6), 40.48(C_{10}), 34.72(C_7), 32.98-(C_8), 31.42(-CH_3), 28.72(-CH_3), 28.49(-CH_3), 18.84(C_9). MS: *m*/*z* 316($M^+ + 2$, 6), 315($M^+ + 1$, 5), 314(M^+, 25), 301(38), 300(20), 299(96), 289(15), 288(18), 287(9), 286(35), 271(23), 251(9), 165(13), 163(9), 162(58), 148(13), 147(100). Anal. Calcd for $C_{20}H_{23}ClO$: C, 76.30; H, 7.36. Found: C, 76.21; H, 7.41.

7,11,11-Trimethyl-5(furan-2-yl)-tricyclo[5.4.0.0^{3,6}]undec-1-ene-4-one (5f). Colorless viscous material, yield 60%. IR ($CHCl_3$)/cm^{-1}: 1777(s), 1565(m), 1500(m), 1462(m), 1453(m), 1435(w), 1367(m), 1214(m), 826(w). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.41(d, 1H, $J = 1.8$ Hz, $C_{4'}$-H), 6.35(dd, 1H, $J = 3.1$, 1.8 Hz, $C_{3'}$-H), 6.05(d, 1H, $J = 3.1$ Hz, $C_{2'}$-H), 5.38(br d, 1H, $J = 2.2$ Hz, C_2-H), 4.51(dd, 1H, $J_{5,6} = 6.8$, $J_{3,5} = 3.1$ Hz, C_5-H), 4.15−4.03(m, 1H, C_3-H), 2.65 (t, 1H, $J\sim 6.3$ Hz, C_6-H), 1.86−1.49(m, 6H, 3 × -CH_2), 1.27 (s, 3H, -CH_3), 1.17 (s, 3H, -CH_3), 1.15 (s, 3H, -CH_3). MS: *m*/*z* 271($M^+ + 1$, 8), 270(M^+, 25), 269(17), 256(24), 255(37), 254(14), 242(8), 241(31), 240(22), 239(7), 227(10), 226(15), 170(8), 169(89). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.88; H, 8.27.

General Procedure for Irradiation of 1,7,7-Trimethyl-3-(*E*-2′-arylethenyl)-oxabicyclo[4.4.0]-deca-3,5-dienes (3a−e) in Aqueous Methanol, Recording of the ^{1}H NMR Spectra of the Crude 11-(*exo*)-Aryl-1,7,7-trimethyl-tricyclo-[4.4.0.1^{2,4}]undec-5-en-3-ones (8a−c), and Isolation of 8d,e. Solutions of **3a**−**e** (400 mg) in a mixture of methanol (250 mL) and water (5 mL) were irradiated under above said conditions. The photolyzate was concentrated under vacuum, and the ^{1}H NMR spectrum of the crude oily residue was recorded. In the case of photolyzates derived from **3d**,**e**, the residual oil when triturated with hexane yielded solids, which were recrystallized from hexane to obtain pure **8d,e**, for which complete spectroscopic data was collected.

11-(*exo*)-*p*-Phenyl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]-undec-5-en-3-one (8a). ^{1}H NMR ($CDCl_3$, 200 MHz, based on the spectrum of crude photolyzate): δ 7.36−7.12(m, arom.-Hs), 5.68(d, 1H, $J = 7.6$ Hz, C_5-H), 3.28(t, 1H, $J \approx 8.1$ Hz, C_4-H), 3.15(s, 1H, C_{11}-H), 2.74(d, 1H, $J = 8.5$ Hz, C_2-H), 1.89−0.82-(overlapping multiplets with sharp singlets at δ1.41, 1.16, 1.12).

1- (*exo*)-*p*-Tolyl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-one (8b). ^{1}H NMR ($CDCl_3$, 200 MHz, based on the spectrum of crude photolyzate): δ 7.10(s, 4H, arom.-Hs), 5.97-(d, 1H, $J = 7.8$ Hz, C_5-H), 3.29(t, 1H, $J \approx 8.1$ Hz, C_4-H), 3.11-(s, C_{11}-H), 2.77(d, $J_{2,4} = 8.4$ Hz, C_2-H), 2.29(s, 3H, -PhCH_3), 1.86−0.87(overlapping multiplets with sharp singlets at δ 1.40, 1.15, 1.09).

11-(*exo*)-*p*-Anisyl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-one (8c). ^{1}H NMR ($CDCl_3$, 200 MHz, based on the spectrum of crude photolyzate): δ 7.15−7.03(m, arom.-Hs), 6.88−6.72(m, arom.-Hs), 5.97 (d, 1H, $J = 7.8$ Hz, C_5-H), 3.78-(s, 3H, −OCH_3), 3.28(t, 1H, $J \approx 8.1$ Hz, C_4-H), 3.11(s, 1H, C_{11}-H), 2.70(d, $J_{2,4} = 8.3$ Hz, C_2-H), 1.93−1.00(broad multiplet with sharp singlets at δ1.40, 1.15, 1.11).

11-(*exo*)-*p*-Bromophenyl-1,7,7-trimethyl-tricyclo-[4.4.0.1^{2,4}]undec-5-en-3-one (8d). Colorless solid, yield 80%, mp 108−109 °C (hexane). IR (KBr)/cm^{-1}: 1770.5(C═O), 1593(s), 1491(s), 1460(m), 1421(w), 1393(w), 1375(w), 1361(m), 1242(w), 1221(w), 1190(w), 1150(w), 1105(w), 1043(m−s), 1071(m−s), 1009(s), 978(w), 895(m), 864(w), 837(w), 810(s), 769(w), 703(w), 669(m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41(d, 2H, $J = 8.4$ Hz, arom.-Hs), 7.08(d, 2H, $J = 8.4$ Hz, arom.-Hs), 5.97(d, 1H, $J = 7.8$ Hz, C_5-H), 3.25(t, 1H, $J = 8.0$ Hz, C_4-H), 3.09(s, 1H, C_{11}-H), 2.75(d, 1H, $J_{2,4} = 8.5$ Hz, C_2-H), 1.93−1.78(m, 2H, -CH_2), 1.65−1.52(m, 2H, -CH_2), 1.42−1.29(m, 2H, -CH_2), 1.40(s, 3H, -CH_3), 1.14(s, 3H, -CH_3), 1.10(s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 203.27(C═O), 150.78(C_6), 140.06(q. arom.), 131.77-(CH), 128.59(CH), 124.74 (C_5), 120.64(q. arom.), 76.78(C_4), 61.59(C_{11}), 52.12(C_7), 43.46(C_2), 41.89(C_8), 38.86(C_{10}), 35.97-(C_1), 31.77(-CH_3), 27.56(-CH_3), 26.15(-CH_3), 18.86(C_9). MS: *m*/*z* 361($M^+ + 2$, 3), 360($M^+ + 1$, 14), 359(M^+, 10), 358(16), 345(74), 344(16), 343(71), 332(16), 330(16), 318(24), 317(85), 316(25), 315(85), 283(18), 261(40), 259(24), 248(23), 247(47), 245(45), 237(29). Anal. Calcd for $C_{20}H_{23}BrO$: C, 66.86; H, 6.45. Found: C, 66.78; H, 6.37.

11-(*exo*)-*p*-Chlorophenyl-1,7,7-trimethyl-tricyclo-[4.4.0.1^{2,4}]undec-5-en-3-one (8e). Colorless solid, yield 80%, mp 140−141 °C (hexane). IR (KBr)/cm^{-1}: 1770.5(C═O), 1595(br), 1495(s), 1458(m), 1420(w), 1375(m), 1363(s), 1352(w), 1242(w), 1221(w), 1190(w), 1150(w), 1107(m), 1090(m), 1045(m−s), 1015(m−s), 978(w), 895(m), 864(w), 839(w), 812(s), 773(m), 704(w), 663(m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.29 (d, 2H, $J = 8.4$ Hz, arom.-Hs), 7.16 (d, 2H, $J = 8.4$ Hz, arom.-Hs), 5.99 (d, $J = 7.7$ Hz, C_5-H), 3.27 (t, $J \approx 8.1$ Hz), 3.14 (s, 1H, C_{11}-H), 2.78 (d, $J_{2,4} = 8.4$ Hz, C_2-H), 1.90−1.84(m, 2H, -CH_2), 1.67−1.26 (m, 4H, 2 × -CH_2 with a sharp singlet, 3H at δ 1.42, -CH_3), 1.16 (s, 3H, -CH_3), 1.12 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 203.39(C═O), 150.78(C_6), 139.53(q. arom.), 132.59-(q. arom), 128.83(CH), 128.23(CH), 124.75(C_5), 76.81(C_4), 61.66(C_{11}), 52.17(C_7), 43.39(C_2), 41.89(C_8), 38.86(C_{10}), 35.97-(C_1), 31.78(-CH_3),), 27.56(-CH_3),), 26.18(-CH_3), 18.86(C_9). MS: *m*/*z* 316($M^+ + 2$, 7), 315($M^+ + 1$, 6), 314(M^+, 28), 301(34), 300(22), 299(97), 289(12), 288(15), 286(37), 271(21), 162(61), 148(19), 147(100). Anal. Calcd for $C_{20}H_{23}ClO$: C, 76.30; H, 7.36. Found: C, 76.21; H, 7.41.

Conversion of 11-(*exo*)-Aryl-1,7,7-trimethyl-tricyclo-[4.4.0.1^{2,4}]undec-5-en-3-ones (8d,e) to 5-Aryl-7,11,11-trimethyl-tricyclo[5.4.0.0^{3,6}]-undec-1-ene-4-ones (5a,e) on Silica Gel. *exo*-11-Aryl-1,7,7-trimethyl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**8d,e**, 200 mg) were stirred with silica gel (5 g) in chloroform (30 mL) for 3 h, when TLC monitoring indicated their complete consumption. Solvent was distilled off from the reaction mixture under reduced pressure. Column chromatography over silica gel (Acme Synthetic Chemicals, Mumbai, India, 60−120 mesh, 5 g, columns packed in hexane) using hexane−chloroform as eluant yielded **5d,e** quantitatively.

General Procedure for Irradiation of Arylidene-β-ionones (1a−f) in Aqueous Methanol and Isolation of 9c,f. Solutions of **1a**−**f** (400 mg) in a mixture of methanol (250 mL) and water (5 mL) were irradiated for 3.5 h. The photolyzates were concentrated under vacuum, and products were extracted with hexane. ^{1}H NMR spectrum of the crude oily residues derived from **1a,b,d,e** showed the presence of only **8a−f,** respectively. However, in case of the photolyzates derived from **1c**,**f**, the ^{1}H NMR spectrum of the crude oily residues indicated the presence of some other photoproduct to the extent of 55% in case of photoltsyate derived from **1c** and 80% in case of **1f**, respectively.

Column chromatographic (silica gel 100−200 mesh, 30 g, packed in hexane) separation of the photolyzate derived from **1c** (hexane−chloroform 95:5, eluent) yielded **5c** (40%) and **12-(*exo*)-*p*-anisyl-8,8-dimethyl-tricyclo[5.4.0.1^{3,6}]dodec-1(7)-ene-4-one (9c)** (55%) as colorless oil. IR ($CHCl_3$)/cm^{-1}: 3517(m), 2940(s), 2043(w), 1893(w), 1872(w), 1739(s), 1662(s), 1619(s), 1590(m), 1568(w), 1547(w), 1521(s), 1470(s), 1449(s), 1410(w), 1393 (w), 1367(m), 1312(w), 1295(w), 1269(s), 1184(s), 1140(m), 1119(m), 1043(s), 948(m), 906(m), 863(w), 837(s), 803(w), 794-(m), 782(m), 765(w), 735(w), 713(w), 683(m), 670(m), 645(w), 602(w), 563(m), 534(m), 491(m), 474(m), 453(m), 444(m), 431(m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.04(dd, 2H, $J = 6.7$, 2.0 Hz, arom.-Hs), 6.82(dd, 2H, $J = 6.7$, 2.0 Hz, arom.-Hs), 3.78(s, 3H, -OCH_3), 3.29 (br s, $J_{3,12} \approx J_{6,12} \approx 0$, 1H, C_{12}-H), 2.85(br d, 1H, $J_{3,2a} = 5.7$ Hz, $J_{3,2b} \approx 0$, C_3-H), 2.78(br d, 1H, $J_{6,5a} = 6.4$ Hz, $J_{6,5b} \approx 0$, C_6-H), 2.45(dd, 1H, $J_{2a,2b} = 15.7$, $J_{3,2a} = 5.7$ Hz, C_2-H_a), 2.27(dd, 1H, $J_{5a,5b} = 17.8$ Hz, $J_{6,5a} = 6.4$ Hz, C_5-H_a), 2.17 (d, 1H, $J = 15.7$ Hz, C_2-H_b), 2.01(dd, $J = 17.8$, 1.8 Hz, C_5-H_b), 1.88−1.81 (m, 2H, C_{11}-Hs), 1.67−1.44 (m, 2H), 1.43−1.34(m, 2H), 1.12(s, 3H, -CH_3), 0.96(s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 220.11(C_4), 158.32($C_{4'}$), 143.53 (C_7), 134.51($C_{1'}$), 127.92($C_{2'}$, $C_{6'}$), 124.88(C_1), 114.09($C_{3'}$, $C_{5'}$), 55.22(-OCH_3), 49.79(C_3), 49.64(C_{12}), 44.77(C_5), 39.80(C_6), 39.23(C_9), 37.55(C_2), 34.45(C_8), 29.97(C_{11}), 27.82, 27.64(2 × -CH_3), 19.41(C_{10}). MS: *m*/*z* 311($M^+ + 1$), 310(M^+), 296(6), 253(5), 192(9), 171(9), 162 (12), 161(100). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.16; H, 8.49.

Similarly, column chromatographic (silica gel 100−200 mesh, 30 g, packed in hexane) separation of the photolyzate derived from **1f** (hexane-chloroform eluent) yielded **5f** (10%) and **12-(*exo*)-(furan-2-yl)-8,8-dimethyl-tricyclo[5.4.0.1^{3,6}]dodec-1(7)-ene-4-one (9f)** (80%) as colorless oil. IR ($CHCl_3$)/cm^{-1}: 2924(s), 2854(s), 2362(m), 1743(s), 1560(w), 1539(w), 1508(w), 1464(m), 1456(m), 1438(w), 1411(w), 1363(m), 1216(m), 823(w), 758(s), 667(w). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.41(d, 1H, $J = 1.8$ Hz, $C_{4'}$-H), 6.35(dd, 1H, $J = 3.1$, 1.8 Hz, $C_{3'}$-H), 6.05(d, 1H, $J = 3.1$ Hz, $C_{2'}$-H), 3.33(br s, $J_{3,12} \approx J_{6,12} \approx 0$, 1H, C_{12}-H), 3.09(d, 1H, $J_{6,5a} = 6.2$ Hz, $J_{6,5b} \approx 0$, C_6-H), 2.83(d, 1H, $J_{3,2a} = 5.50$ Hz, $J_{3,2b} \approx 0$, C_3-H), 2.56(dd, 1H, $J_{2a,2b} = 15.88$, $J_{3,2a} = 5.5$ Hz, C_2-H_a), 2.35(dd, 1H, $J_{5a,5b} = 18.6$, $J_{6,5a} = 6.2$ Hz, C_5-H_a), 2.15(overlapping dds, 2H, C_2-H_b, C_5-H_b), 1.82(m, 2H, C_{11}-Hs), 1.74−1.56(m, 2H), 1.43−1.34(m, 2H), 1.11(s, 3H, -CH_3), 1.00(s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 220.96(C_4), 156.56($C_{1'}$), 143.14(C_7), 142.18($C_{4'}$), 125.32(C_1), 110.60($C_{2'}$), 106.04($C_{3'}$), 49.98(C_3), 45.80(C_5), 45.18(C_{12}), 39.57(C_9), 36.98(C_2), 36.69(C_6), 34.75(C_8), 30.28(C_{11}), 28.05, 27.87(2 × -CH_3), 19.63(C_{10}). MS: *m*/*e* 271($M^+ + 1$, 10), 270(M^+, 21), 269(19), 256(26), 255(39), 254(11), 242(10), 241(33), 240(26), 226(17), 169(87), 111(46), 98(15), 97(21), 96(21), 94(29), 93(28) 79(50). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.87; H, 8.27.

Supporting Information Available: X-ray crystallographic data including ORTEP diagram for compound **5b**, details of instrumental analysis, and NMR spectra including 2D NMR spectra for compounds **9c,f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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