Photochemical Reorganisation of 1,7,7-Trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]deca-3,5-dienes

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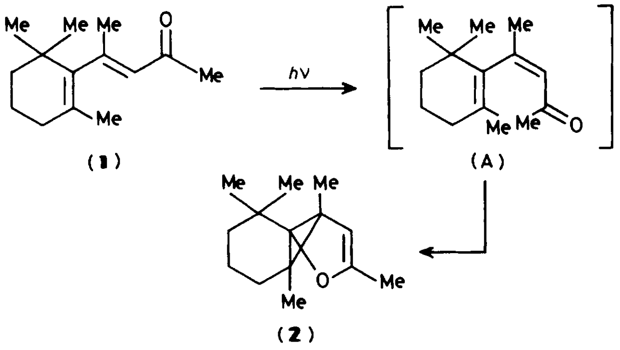
A novel photochemical conversion of 1,7,7-trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]deca-3,5-dienes (**6a—c**) into the corresponding *endo*-1,7,7-trimethyl-11-aryl-tricyclo[4.4.0.1^{2,4}]undec-5-en-3-ones (**7a—c**) in high yield (75—80%) is reported.

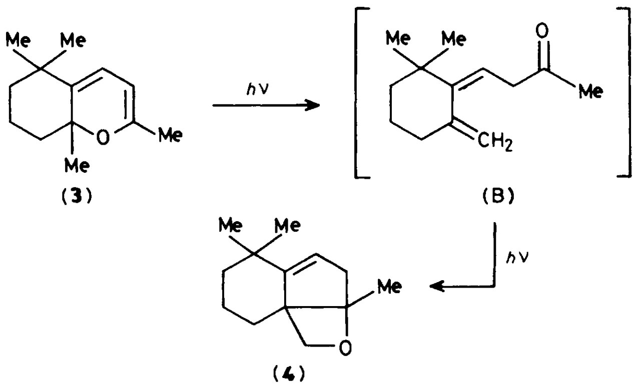
(*E*)-β-Ionone has been reported to display 3 prominent modes of photoreaction involving the dienone moiety, namely, *E*/*Z* isomerisation, 6π electrocyclisation to form 2H pyran, and conversion into (*Z*)-retro-γ-ionone through a 1,5-H shift.[1—4] However, Jeger *et al.*,[5] have recently observed that (*E*)-7-methyl-β-ionone (**1**), on photolysis in pentane, produces the tricyclic compound (**2**) (66% yield) involving, presumably, the participation of (*Z*)-7-methyl-β-ionone (A) as an intermediate. Again, Cerfontain *et al.*,[6] have reported that direct irradiation, in ethanol, of both (*E*)-β-ionone and the corresponding 2H pyran (**3**) leads eventually to the tricyclic oxetane (**4**), albeit in low yield, through intervention of (*Z*)-retro-γ-ionone (B).

Here we describe the photolability of 1,7,7-trimethyl-3-(*E*-2′-arylethenyl)-2-oxabicyclo[4.4.0]deca-3,5-dienes (**6a—c**) which were obtained from photolysis of the corresponding *E*/*E*-arylidene-β-ionones (**5a—c**);† the 2*H*-pyrans (**6a—c**), on short-time irradiation in aqueous methanol, undergo a remarkable further transformation.

In a typical experiment, when a solution of (**6a**) (0.4 g) in 250 ml of methanol–H_2O (4 : 1) was photolysed (pyrex filter) with a 125 W medium pressure Hg arc for 3.5 h and the photolysate chromatographed (silica gel, hexane–benzene, 95 : 5 eluant) 0.32 g of *endo*-1,7,7-trimethyl-11-phenyltricyclo-[4.4.0.1^{2,4}]undec-5-en-3-one (**7a**) was obtained [80% yield, colourless crystals (hexane), m.p. 75—76 °C]. Its gross structure was determined from mass, i.r. ^{13}C n.m.r., and ^1H n.m.r. spectra.‡ The stereochemical relationship of hydrogens around the 4-ring and *endo*-orientation of the phenyl group in (**7a**) were ascertained from the value of vicinal coupling constants, $J_{11,2} = J_{11,4}$ 6.3 Hz, which could be determined using double resonance experiments involving C_{11}-H, C_4-H and C_2-H.§



Irradiation of the pyrans, (**6b**) and (**6c**), in methanol–H_2O under the above conditions for 3.5 h each led to the respective tricyclic ketones, (**7b**) [75% yield, m.p. 60—61° C (methanol)] and (**7c**) [80% yield, m.p. 97—98 °C (methanol)]. Similar results were obtained when the pyrans, (**6a—c**) were photolysed in THF–H_2O (THF = tetrahydrofuran), dioxane–H_2O and acetone–H_2O, however, their solutions in anhydrous



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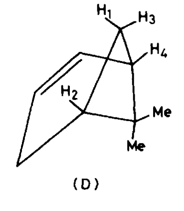
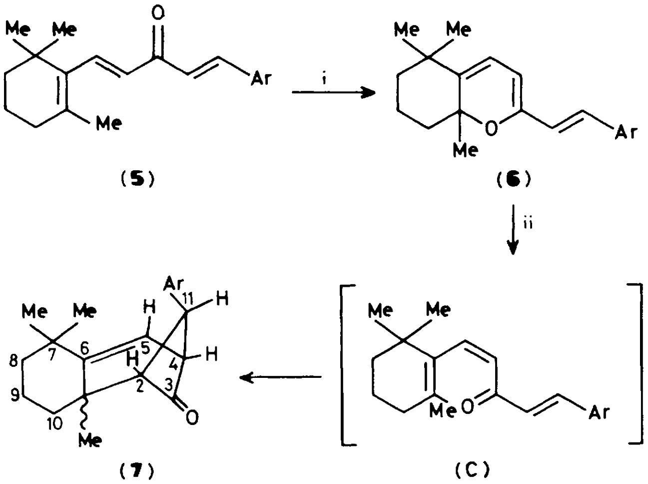
† In a typical reaction, a solution of (**5a**) (2%) in anhydrous thiophene-free benzene was irradiated for 2 h with a 125 W medium pressure Hg lamp and chromatographed (silica gel, hexane eluant) to obtain (**6a**) [90% yield, m.p. 84—85 °C (hexane)]; (**6b**) and (**6c**) were synthesised similarly; (**6b**) [85% yield, m.p. 81—82 °C (hexane)]; (**6c**) (90% yield, m.p. 120—121 °C) and identified through spectral studies (i.r. mass, ^1H n.m.r.): the *E*-geometry in the 3-(2′-arylethenyl) substituent was assigned by ^1H n.m.r. coupling.

‡ *Selected spectral data* for (**7a**): *m*/*z* 280 (M^+); $\nu_{max.}$ (KBr): 1770 (4-ring ketone); ^{13}C n.m.r. δ 201.0 (C=O), 66.4, 62.0, 48.4 (each signal splits into a doublet in SFORD spectrum; 4 ring Cs 2, 4, and 11 respectively), 149.2 (no splitting in SFORD spectrum, C_6); ^1H n.m.r., δ 1.30—2.30 (envelope), 1.18 (s, 6H, C_7-Me), 1.31 (s, 3H, C_1-Me), 2.65 (t, C_{11}-H, $J_{11,2} = J_{11,4}$ 6.3 Hz), 3.98 [quintet, C_4-H, $J_{4,5}$ 2.2 Hz, $J_{4,2}$ (LR) 3.0 Hz], 4.40 [dd, C_2-H, $J_{2,11}$ 6.3 Hz, $J_{2,4}$ (LR) 3.0 Hz], 5.44 (d, C_5-olefinic H, $J_{5,4}$ 2.2 Hz), 7.2 (br.s, phenyl); the coupling constants, $J_{11,2}$ $J_{11,4}$, $J_{2,4}$, became available through irradiation of resonances at δ 2.65 (C_{11}-H), 3.98 (C_4-H) and 4.4 (C_2-H). Similar spectral data were obtained for (**7b**) and (**7c**).

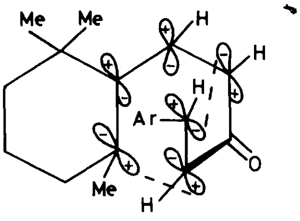
§ The observed *J* values are reminiscent of vicinal couplings,[7] $J_{3,2} = J_{3,4}$ 5.7 Hz, in bicyclo[3.1.1]heptene derivative (D).



(D)



Scheme 1. *Conditions*: i, *h*v, pyrex, benzene, 30 min, 25 °C; ii, *h*v, pyrex, MeOH–H_2O, 3.5 h, 25 °C.



(T)

a, Ar = Ph
b, Ar = C_6H_4Me-*p*
c, Ar = C_6H_4OMe-*p*

benzene, THF, dioxane, and acetone were found to be stable to u.v. light for several hours.

Apparently, the above photoconversion of the pyrans (**6**) into the tricyclic ketones (**7**) requires passage through the respective arylidene-β-ionones (C) or their respective adducts with H_2O (ketone-hydrate ?); the latter presumably undergo a symmetry-allowed intramolecular $\Pi_a{}^4 + \Pi_s{}^2$ cycloaddition reaction involving a transition state such as (T).¶

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¶ This stereomode of addition is supported by molecular models of the transition state (T). However, the stereochemistry of C_1-Me is yet unclear, albeit, considerations of (T) suggest this to be β-oriented.