ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 141 (2001) 133–138

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

The photochemistry of 1-cyclohexenyl-2,4,6-trimethylphenyl-methanone (1-mesitoyl-cyclohexene)

Abd El-Aal M. Gaber*,[1], Ingeborg Heise, Johannes Leitich[2], Kurt Schaffner

Max-Planck-Institut für Strahlenchemie, Postfach 101365, D-45413 Mülheim an der Ruhr, Germany

Received 22 January 2001; accepted 1 April 2001

Abstract

The photochemistry (direct irradiation in solution, $\lambda > 300$ nm) of the title compound (**8**) has been investigated. Whereas, in contrast to the methyl-free analog of **8**, only undefined material of higher molecular weight was obtained upon irradiation without additives in acetonitrile and toluene, this situation changed dramatically in the presence of co-reactants. Thus, in ethyl vinyl ether, [4+2] adducts **11a** and **11b** were obtained in good combined yield. In acetonitrile, in the presence of acid which catalyses a skeletal rearrangement, the hexahydrofluorenone **14** was the main product. The results point to the intermediacy of the *trans*-cyclohexene isomer of **8**, viz. **9**, and to the 2-oxyallyl **10** as consecutive intermediates, in analogy to the methyl-free system. The molecular structures of some unprecedented minor by-products such as **15a–c** even more clearly reveal their origin from **10**. Photoreactions of **8** in the presence of either water or phenol as co-reactants proceeded less cleanly but did give defined products such as **16–18** in moderate yields. © 2001 Published by Elsevier Science B.V.

Keywords: *Trans*-1-cyclohexenyl aryl ketone; 2-Oxyallyl; Photoisomerisation

1. Introduction

In 1972, Smith and Agosta [1] found that the irradiation of 1-cyclohexenyl-phenyl-methanone (**1**), of which the title compound is a trimethyl derivative, gave hexahydrofluorenone **5**. Subsequently, by isolation of compounds **6** and **7**, by spectroscopic detection of **4**, by chemical trapping of intermediates **2** and **3** by added cyclopentadiene, and by studying product ratios and relative quantum yields, we established the mechanism of this reaction as given in Scheme 1 [2]. This reaction mechanism was corroborated by chemical trapping of **2** by added enol ethers to give Diels–Alder adducts in good yields and, again, by studying product ratios and relative quantum yields [3].

Smith and Agosta [1] noted that the irradiation of the title compound, 1-cyclohexenyl-2,4,6-trimethylphenyl-methanone (**8**, Scheme 2), under conditions that cleanly transformed **1** to **5** gave no monomeric product. We confirm this observation; the oligomeric product mixture that we obtained from **8** under standard irradiation conditions ($\lambda > 300$ nm, acetonitrile or toluene) was so complex that its ^{1}H-NMR spectrum showed only a broad envelope with no perceivable methyl singlets. Since no reason can be seen why the intermediates **9** and **10** should not form as readily as their methyl-free counterparts **2** and **3**, the obvious cause for this difference in behaviour is that **10** cannot readily give the rearrangement analogous to **3** → **4** since it bears a methyl group where **3** bears a hydrogen atom that must be eliminated on passage to **4**. Thus, lacking easily accessible unimolecular exit channels, **10** probably reacts with itself or with **9**.

It occurred to us that this situation might be changed if the photolysis of **8** was carried out in the presence of trapping agents for **9** and **10** which could transform these intermediates into isolable adducts. Also, we recalled that we had found the transformation **3** → **5** to be strongly accelerated by added acid [2]; one can conceive a similar profitable effect of acid on **10**. Under such circumstances, the irradiation of **8** might prove as useful for synthetic purposes as that of **1**. In the following section, we report experiments that verify this concept.

2. Experimental

2.1. General aspects and methods

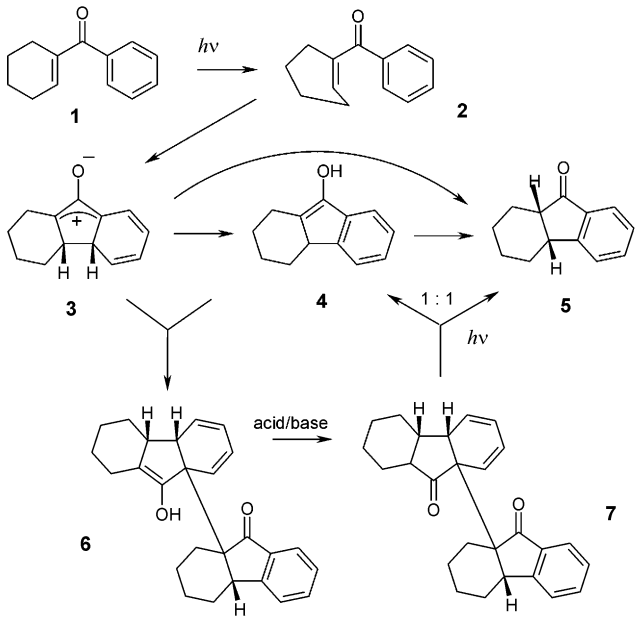
For general aspects and methods, see our previous publications [2,3].

* Corresponding author.

[1] On leave from Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt, in 1999.

[2] Co-corresponding author. Fax: +49-208-3063951.

1010-6030/01/$ – see front matter © 2001 Published by Elsevier Science B.V.
PII: S1010-6030(01)00458-0



Scheme 1.

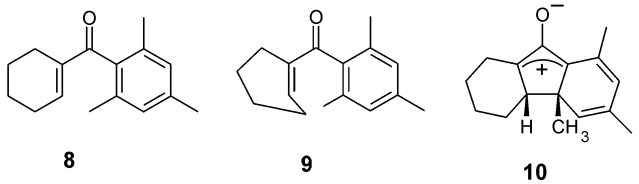
Irradiations. Immersion well apparatus (50 or 100 ml, solidex glass) allowing evacuation, with a central 125-W high-pressure mercury lamp (Philips HPK 125), magnetic stirring, argon atmosphere after degassing the reactant solution, tap water as coolant, ambient temperature.

Preparative chromatography. Silica gel Merck, 0.040–0.063 mm.

Multiplicities are not reported in the following for NMR signals if their multiplicities are as expected for the positions assigned.

2.2. Elucidation of molecular structures

A combination of NMR techniques (400 MHz-^{1}H, ^{13}C-BB and −DEPT, short-range (1 bond) and long-range (2–3 bonds) ^{13}C/^{1}H correlation, ^{1}H/^{1}H spin decoupling, ^{1}H/^{1}H NOE) allowed the complete elucidation of the molecular structures including the stereochemistry of compounds such as **8**, **11a**,**b**, **13a**,**b**, **14**, **15a–c**, **16**, **17**, and **18**. The relative configuration at C-4a/4b in **15a**,**b** was inferred from the similarity of the ^{1}H NMR δ and J values to those of **15c**, the configuration of which has been established by ^{1}H/^{1}H NOE measurements.



Scheme 2.

2.3. (Trans-2-chlorocyclohexyl)-2,4,6-trimethylphenyl-methanone and 1-cyclohexenyl-2,4,6-trimethylphenyl-methanone (*8*)

A 500 ml three-necked flask was flushed with argon and charged with 38 g (0.274 mol) of anhydrous zinc chloride and 300 ml of redistilled dichloromethane and cooled to 0°C (*Kondakov* reaction conditions [4–7]). 49.6 g (0.272 mol) of 2,4,6-trimethyl-benzoyl chloride (mesitoyl chloride [8]) was added under stirring. After 30 min of stirring, the contents of the flask were again cooled to 0°C. 46 g (0.56 mol) of cyclohexene was added dropwise while keeping the temperature below 10°C whereupon the mixture turned yellow. Stirring at 10°C was continued over-night. 160 ml of water was added dropwise under stirring while keeping the temperature below 15°C. More water was added without precautions, the two liquid phases were separated, the water phase was extracted with 300 ml of dichloromethane, the combined dichloromethane phases were successively washed with water, dilute aqueous sodium hydroxide, and water, and dried over anhydrous sodium sulphate. Distillation of the residue of dichloromethane phases yielded, after lower boiling material, 40.6 g (56.5%) of a fraction, b.p. 124–170°C at 0.005 mbar, according to ^{1}H NMR, mainly (trans-2-chlorocyclohexyl)-2,4,6-trimethylphenyl-methanone with some **8**. This material was used without purification in the following step. Pure (trans-2-chlorocyclohexyl)-2,4,6-trimethylphenyl-methanone, m.p. 79–82°C could be obtained from it by a single crystallisation from ether/pentane at −23°C. It remained unchanged in refluxing triethylamine.

^{1}H NMR ($CDCl_3$): δ = 6.82 (s; 2 H), 4.34 (ddd, J = 11.3, 10.1, and 4.3 Hz; 1 H), 3.14 (ddd, J = 11.3, 10.3, and 4.0 Hz; 1 H), 2.32 (m; 1 H), 2.28 (s; 6 H), 2.26 (s; 3 H), 1.95 (m; 1 H), 1.75 (mc; 3 H), 1.30 (mc; 3 H).

^{13}C NMR ($CDCl_3$): 208.0 (C), 139.0 (C), 137.4 (C), 134.6 (2 C) 129.0 (2 CH), 59.3 (CH), 58.4 (CH), 36.3 (CH_2), 29.6 (CH_2), 25.6 (CH_2), 24.9 (CH_2), 21.0 (CH_3), 20.1 (2 CH_3).

3.55 g (0.154 g-at.) sodium metal was dissolved in 550 ml ethanol. To the stirred solution at room temperature, 40.6 g of crude material obtained above was added and stirring at room temperature was continued for 1 h (more prolonged exposure to sodium ethoxide caused complete decomposition of the desired product). Evaporation of the solvent i.v., distribution of the residue between ether and water, drying the ether layer, and evaporation of the ether, left a residue that was distilled to give 32.3 g, b.p. 96–112°C at 0.002 mbar. Fractional crystallisation from ether/pentane at −23°C gave 22.6 g of **8**. Chromatography of the mother liquor (750 g silica gel, pentane + 2% ether) gave, after material that was discarded, 5.4 g of a fraction that upon crystallisation yielded 4.0 g of **8**. Combined yield of **8**, m.p. 43–45°C, was 26.6 g (42.9% overall yield based on mesitoyl chloride).

^{1}H NMR ($CDCl_3$): δ = 6.80 (s; 2H), 6.47 (tt; $J = 2 \times 4.0$ and 2×1.7 Hz; 1 H), 2.37 (m; 2 H), 2.26 (s; 3H), 2.15 (m; 2 H), 2.08 (s; 6 H), 1.69 (m; 2 H), 1.62 (m; 2 H).

^{13}C NMR ($CDCl_3$): 202.2 (C), 145.2 (CH), 140.3 (C), 137.7 (C), 137.5 (C), 134.1 (2 C), 128.0 (2 CH), 26.3 (CH_2), 22.4 (CH_2), 21.9 (CH_2), 21.7 (CH_2), 21.0 (CH_3), 19.1 (2 CH_3).

2.4. (3α,4aα)- and (3α,4aβ)-3-Ethoxy-4,4a,5,6,7,8-hexahydro-1-(2,4,6-trimethylphenyl)-3H-isochromene (**11a** and **11b**), and (cis- and trans-2-(Z-2-ethoxy-vinyl)-cyclohexyl)-(2,4,6-trimethylphenyl)-methanone (**13a** and **13b**)

1000 mg (0.438 mol) of **8** in 50 ml ethyl vinyl ether was irradiated for 13 h after which time 87.8% of **8** had reacted whereby 61.5 and 11.5% of the reacted **8** were transformed into **11a,b** and **12**, respectively (^{1}H NMR of the crude reaction product). Evaporation of the ethyl vinyl ether and chromatography of the residue over 200 g silica gel using pentane + 1% diethyl ether as the eluent yielded consecutively: 10.7 mg unidentified mixture, 368.2 mg (31.9%) **11a**, 203.1 mg (17.6%) **11b**, (continued with pentane + 3% diethyl ether) 53.6 mg unidentified mixture, 122 mg **8**, 66.7 mg (5.8%) **13a**, 20.7 mg (1.8%) of a (34.5:6.5:23:36) mixture of **13a**, **13b**, and the *E* stereoisomers of **13a** and **13b**, respectively, and 28.7 mg (2.5%) **13b**, whereupon the elution was discontinued. All compounds were liquids.

NMR data (for the numbering of positions in **11a**,**b** see our previous paper [3]):

11a. ^{1}H NMR ($CDCl_3$): δ = 6.915 and 6.911 (2s; 2 *ar*-H), 5.10 (3-eq), 3.96 and 3.60 (O-CH_2), 2.40 (4a-ax), 2.36, 2.33, and 2.27 (3 *ar*-CH_3), 2.11 (4-eq-H), 1.98 (6-eq-H), 1.97 (5-eq-H), 1.96 (7-eq-H), 1.92 (8-eq-H), 1.79 (8-ax-H), 1.72 (4-ax-H), 1.41 (6-ax-H), 1.28 (ethyl-CH_3), 1.17 (7-ax-H), 1.14 (5-ax-H). Selected $J_{H,H}$ values (Hz): 3.6 (3-eq-H, 4-eq-H), 2.2 (3-eq-H, 4-ax-H), 13.1 (4-eq-H, 4-ax-H), 6.4 (4-eq-H, 4a-ax-H).

^{13}C NMR ($CDCl_3$): δ = 139.7 (C-1), 137.05, 137.02, 136.7, and 132.5 (4 *ar*-C), 127.76 and 127.65 (2 *ar*-CH), 113 (C-8a), 96.3 (C-3), 63.4 (O-CH_2), 35.6 (C-4), 34.7 (C-5), 29 (C-4a), 27.9 (C-8), 26.9 (C-7), 26 (C-6), 21, 19.3, and 18.7 (3 *ar*-CH_3), 14.9 (ethyl-CH_3).

11b. ^{1}H NMR ($CDCl_3$): δ = 6.83 and 6.82 (2s; 2 *ar*-H), 4.90 (3-ax–H), 3.90 and 3.51 (O-CH_2), 2.27 (4a-ax-H), 2.29, 2.25, and 2.15 (3 *ar*–CH_3), 2.13 (4-eq-H), 1.92 (5-eq-H), 1.85 (8-eq-H), 1.73 (6-eq-H), 1.64 (4-ax-H), 1.62 (8-ax-H), 1.60 (7-eq-H), 1.27 (6-ax-H), 1.19 (ethyl-CH_3), 1.14 (5-ax- and 7-ax-H). Selected $J_{H,H}$ values (Hz): 2 (3-ax-H, 4-eq-H), 8.8 (3-ax-H, 4-ax-H), 13.1 (4-eq-H, 4-ax-H), 7 (4-eq-H, 4a-ax-H), 8.8 (4-ax-H, 4a-ax-H).

^{13}C NMR ($CDCl_3$): δ = 140.9 (C-1), 137.19, 137.14, 136.9, and 132.5 (4 *ar*-C), 127.8 and 127.7 (2 *ar*-CH), 113 (C-8a), 99.3 (C-3), 64.2 (O-CH_2), 37.1 (C-4), 34.7 (C-5), 34.6 (C-4a), 28.2 (C-8), 26.7 (C-7), 26.1 (C-6), 21.1, 19.5, and 19.4 (3 *ar*-CH_3), 15.1 (ethyl-CH_3).

13a. ^{1}H NMR ($CDCl_3$): δ = 6.78 (s; 2 *ar*-H), 5.89 (2′-H), 4.71 (1′-H), 3.72 and 3.70 (OCH_2), 3.12 (2-H), 2.98 (1-H), 2.24 (*ar*-CH_3), 2.19 (2 *ar*-CH_3), 1.89 and 1.43 (3-CH_2), 1.46 and 1.40 (4-CH_2), 1.73 and 1.31 (5-CH_2), 1.83 and 1.68 (6-CH_2), 1.18 (ethyl-CH_3). Selected $J_{H,H}$ values (Hz): 3.66 (1-H, 2-H), 10.3 and 3.66 (1-H, 6-CH_2), 2 × 3.7 (2-H, 3-CH_2), 8.5 (2-H, 1′-H), 1.4 (2-H, 2′-H), 6.4 (1′-H, 2′-H).

^{13}C NMR ($CDCl_3$): δ = 212.5 (C=O), 144.3 (C-2′), 139.4 and 138.0 (2 *ar*-C), 134.0 (2 *ar*-C), 128.7 (2 *ar*-CH), 106.3 (C-1′), 67.4 (O-CH_2), 54 (C-1), 32.2 (C-3), 31.6 (C-2), 25 (C-5), 23.5 (C-6), 22.2 (C-4), 20.9 (*ar*-CH_3), 19.5 (2 *ar*-CH_3), 15.3 (ethyl-CH_3).

13b. ^{1}H NMR ($CDCl_3$): δ = 6.78 (s; 2 *ar*-H), 5.79 (2′-H), 4.18 (1′-H), 3.76 and 3.74 (OCH_2), 2.87 (2-H), 2.73 (1-H), 2.24 (*ar*-CH_3), 2.21 (2 *ar*-CH_3), 1.79 and 1.14 (3-CH_2), 1.68 and 1.18 (4-CH_2), 1.62 and 1.30 (5-CH_2), 1.85 and 1.36 (6-CH_2), 1.23 (ethyl-CH_3). Selected $J_{H,H}$ values (Hz): 10.9 (1-H, 2-H), 10.9 and 3.6 (1-H, 6-CH_2), 10.8 and 4.0 (2-H, 3-CH_2), 9.2 (2-H, 1′-H), 6.4 (1′-H, 2′-H).

^{13}C NMR ($CDCl_3$): δ = 11.5 (C=O), 144.3 (C-2′), 138.9 and 138.3 (2 *ar*-C), 134.2 (2 *ar*-C), 128.8 (2 *ar*-CH), 110.6 (C-1′), 67.6 (OCH_2), 56.8 (C-1), 34.5 (C-2), 32.7 (C-3), 28.8 (C-6), 25.8 (C-4), 25.4 (C-5), 21.0 (*ar*-CH_3), 19.8 (2 *ar*-CH_3), 15.3 (ethyl-CH_3).

E-stereoisomer of **13a**: ^{1}H NMR ($CDCl_3$): δ = 6.12 (2′-H), 5.02 (1′-H). $J_{H,H}$ values: 9.25 (2-H, 1′-H), 12.7 (1′-H, 2′-H).

E-stereoisomer of **13b**: ^{1}H NMR ($CDCl_3$): δ = 6.30 (2′-H), 4.62 (1′-H). $J_{H,H}$ values: 9.0 (2-H, 1′-H), 12.7 (1′-H, 2′-H).

2.5. 4aα,9aα-5,6,8-Trimethyl-1,2,3,4,4a,9a-hexahydro-fluoren-9-one (**14**) and 7-hydroxy- and 7-acetoxy-(4aα, 4bα, 7α,9aα)-4b,6,8-trimethyl-1,2,3,4,4a,4b,7,9a-octahydro-fluoren-9-one (**15a** and **15b**)

A solution of 1500 mg (6.58 mmol) of **8** in a mixture of 10 ml acetic acid and 90 ml acetonitrile was irradiated for 15 h after which time no further reaction took place even though not all **8** had reacted; the solution had turned orange. Evaporation of solvent, dissolution of the residue in ether, washing the ether solution with aqueous sodium bicarbonate until free of acetic acid, drying over sodium sulphate, evaporation, and chromatography of the residue over 400 g silica gel using dichloromethane as the eluent yielded consecutively: 31.8 mg of unidentified mixture, 760.7 mg **14**, 292.8 mg **8**, 25.7 mg **14** (sic!), 25.1 mg of unidentified mixture, 41.6 mg **15a**, 49.3 mg unidentified mixture, 47.5 mg **15a** (sic!), (continued with dichloromethane + 5% diethyl ether) 306 mg unidentified mixture. Combined yields (based on unrecovered **8**) of **14** and **15a** were 65.1 and 6.8%, respectively. In some runs, some **15b** was obtained at the expense of **15a**; it eluted shortly before the latter. **14**: m.p. 70–72°C (from ethanol). **15a**,**b**: liquids.

14: ^{1}H NMR ($CDCl_3$): δ = 6.88 (7-H), 3.32 (4a-H), 2.67 (9a-H), 2.54 (8-CH_3), 2.41 (β1-H), 2.27 (6-CH_3), 2.22 (5-CH_3), 2.19 (α4-H), 1.59 (α1-H, α2-H, and β3-H), 1.25 (α3-H), 1.08 (β2-H), 0.71 (β4-H). Selected $J_{H,H}$ values (Hz): 6.34 (4a-H, 9a-H), 11.3 (4a-H, β4-H), 5.8 (4a-H,

α4-H), 6.9 (9a-H, α1-H), 2 (9a-H, β1-H), 2 (9a-H, α4-H). NOE enhancements: 4a-H/9a-H, 4a-H/α4-H, 4a-H/α3-H, 4a-H/5-CH_3, 7-H/6-CH_3, 7-H/8-CH_3, 9a-H/α1-H, 9a-H/β1-H.

^{13}C NMR ($CDCl_3$): δ = 207.9 (C-9), 157.9, 142.8, 135.6, 130.7 and 129.8 (C-4b, -5, -6, -8, -8a), 131.0 (C-7), 49.7 (C-9a), 38.1 (C-4a), 32.3 (C-4), 24 (C-3), 22.8 and 22.6 (C-1 and -2), 20.2 (6-CH_3), 17.7 (8-CH_3), 13.9 (5-CH_3).

15a: ^{1}H NMR ($CDCl_3$): δ = 5.56 (5-H), 3.14 (7-H), 2.64 (9a-H), 2.24 (β1-H), 2.19 (8-CH_3), 1.95 (4a-H), 1.81 (6-CH_3), 1.55 (α4-H), 1.54 (OH), 1.51 (β3-H), 1.43 (α2-H), 1.34 (α1-H), 1.15 (4b-CH_3), 1.01 (α3-H), 0.79 (β2-H), 0.48 (β4-H).

^{13}C NMR ($CDCl_3$): δ = 206.9 (C-9), 147.7 (C-8), 139.1 (C-8a), 133.1 (C-5), 132.7 (C-6), 55 (C-7), 47.0 (C-9a), 45.2 (C-4a), 44.8 (C-4b), 26.6 (C-4), 26.5 (4b-CH_3), 24.5 (C-3), 23.3 (C-1), 22.9 (C-2), 22.85 (6-CH_3), 19.9 (8-CH_3).

15b: ^{1}H NMR ($CDCl_3$): δ = 5.94 (7-H), 5.70 (5-H), 2.70 (9a-H), 2.25 (β1-H), 2.15 (8-CH_3), 2.13 (acetyl-CH_3), 1.99 (4a-H), 1.68 (6-CH_3), 1.60 (α4-H), 1.55 (β3-H), 1.47 (α2-H), 1.39 (α1-H), 1.10 (4b-CH_3), 1.06 (α3-H), 0.84 (β2-H), 0.64 (β4-H).

^{13}C NMR ($CDCl_3$): δ = 206.5 (C-9), 170.9 (COO), 141.8 (C-8), 137.6 (C-8a), 130.6 (C-5), 129.6 (C-6), 71.6 (C-7), 47.8 (C-9a), 44.9 (C-4b), 42.8 (C-4a), 27 (4b-CH_3), 26.9 (C-4), 24.3 (C-3), 23.3 (C-1), 22.8 (C-2), 20.6 (8-CH_3), 18.9 (6-CH_3), 15.2 (acetyl-CH_3).

*2.6. (2α,7α)-7-Hydroxy-1,10,13-trimethyl-tricyclo-[7.2.2.0^{2,7}]trideca-10,12-dien-8-one (**16**)*

A solution of 1000 mg (4.38 mmol) **8** in 32 ml acetonitrile and 16 ml water was irradiated for 20 h. The solution was separated from white polymer and evaporated to leave 548 mg residue which also appeared to be largely polymeric. Chromatography of the residue over 200 g silica gel using pentane + 2% diethyl ether as the eluent yielded consecutively: 6.7 mg unidentified mixture, 3.2 mg (0.32%) **15c**, 4.6 mg (0.46%) **14**, 37.7 (3.77%) **8**, and (continued with pentane + 4% diethyl ether) 41.6 mg (3.86%) **16**.

16: UV (*n*-hexane): λ_{max} (log ε): 286 (2.57), 250 (2.93), 212 nm (3.89).

^{1}H NMR ($CDCl_3$; numbering: 10 and 11 *syn*, 12 and 13 *anti* to −OH): δ = 5.77 (11-H), 5.56 (12-H), 3.81 (OH), 3.28 (9-H), 2.05 (dt; J = 12.5, 12.5, 5.6 Hz; β6-H), 1.96 (t; J = 2 × 5.3 Hz; 2-H), 1.88 (13-CH_3), 1.80 (10-CH_3), 1.74 and 1.64 (3-CH_2), 1.64 and 1.55 (5-CH_2), 1.4 (α4-H), 1.25 (β4-H), 1.15 (1-CH_3), 1.13 (α6-H). NOE enhancements: 1-CH_3/2-H, 1-CH_3/11-H, 1-CH_3/12-H, 2-H/11-H, 2-H/OH, α6-H/β6-H, α6-H/OH, β6-H/12-H, 9-H/10-CH_3, 9-H/13-CH_3, 10-CH_3/11-H, 12-H/β4-H, 12-H/13-CH_3.

^{13}C NMR ($CDCl_3$; numbering: 10 and 11 *syn*, 12 and 13 *anti* to −OH): δ = 200.9 (C-8), 138.6 (C-11), 136.9 and 133.8 (C-10 and -13), 133.4 (C-12), 80.0 (C-7), 61.7 (C-9), 56.7 (C-2), 40.7 (C-1), 35.2 (C-6), 25.0 (C-3), 24.7 (1-CH_3), 21.7 and 21.6 (C-4 and -5), 21.5 (13-CH_3), 19.5 (10-CH_3).

*2.7. (4aα,4bα, 9aα)-4b,6,8- Trimethyl-1,2,3,4,4a,4b,7,9a-octahydro-fluoren-9-one (**15c**), (cis-2-phenoxy-cyclohexyl)-2,4,6-trimethylphenyl-methanone (**17**), and (trans-2-(2-hydroxyphenyl)-cyclohexyl)-2,4,6-trimethylphenyl-methanone (**18**)*

A solution of 2000 mg (8.77 mmol) **8** and 10 g phenol in 100 ml acetonitrile was irradiated for 24 h after which time ca. 60% of **8** had reacted. After evaporation of the acetonitrile, extraction of the ethereal solution of the residue with aqueous sodium hydroxide in order to remove phenol, drying the ethereal solution with anhydrous sodium sulphate, and evaporation of the ether, chromatography of the residue over 200 g silica gel using pentane + 2% diethyl ether as the eluent yielded consecutively: 106 mg unidentified mixture, 25.5 mg (1.26%) **15c**, 14.6 mg (0.73%) **14**, 812 mg (40.6%) **8**, 145 mg (5.13%) **17**, 105.4 mg unidentified mixtures, (continued with pentane + 4% diethyl ether) 136.5 mg (4.83%) **18**, 83.8 mg unidentified mixtures, (continued with pentane + 6% diethyl ether) 54 mg (2.5%) **15a**, 117.1 mg unidentified mixtures.

15c: ^{1}H NMR ($CDCl_3$): δ = 5.46 (5-H), 2.82 and 2.49 (AB-system, J = 22.3 Hz; 7-CH_2), 2.61 (9a-H), 2.25 (β1-H), 2.19 (8-CH_3), 1.93 (4a-H), 1.69 (6-CH_3), 1.60 (α4-H), 1.53 (β3-H), 1.44 (α2-H), 1.36 (α1-H), 1.06 (4b-CH_3), 1.02 (α3-H), 0.83 (β2-H), 0.62 (β4-H). Selected $J_{H,H}$ values (Hz): 6.2 (9a-H, 4a-H), 6.2 (9a-H, α1-H), ∼0 (9a-H, β1-H), 12.4 (4a-H, β4-H), 5.2 (4a-H, α4-H). NOE enhancements: α4-H/5-H, 4a-H/4b-CH_3, 4a-H/5-H, 4a-H/9a-H, 4b-CH_3/5-H, 5-H/6-CH_3, 6-CH_3/α7-H, 6-CH_3/β7-H, 8-CH_3/α7-H, 8-CH_3/β7-H, 9a-H/4b-CH_3, 9a-H/α1-H, 9a-H/β1-H.

^{13}C NMR ($CDCl_3$): δ = 206.8 (C-9), 144.7, 135.7, and 129.4 (C-6, -8, and -8a), 128.2 (C-5), 47.3 (C-9a), 44.8 (C-4b), 43.9 (C-4a), 40.2 (C-7), 27.2 (C-4), 26.5 (4b-CH_3), 24.5 (C-3), 23.3 (C-1), 22.9 (C-2), 22.3 (6-CH_3), 18.5 (8-CH_3).

17: ^{1}H NMR ($CDCl_3$): δ = 7.19 (2 *m*-phenyl-H), 6.88 (*p*-phenyl-H), 6.76 (2 *o*-phenyl-H), 6.75 (s; 3- and 5-mesityl-H), 4.91 (q; J = 3 × 3.0 Hz; 2-H), 2.78 (dt; J = 12.8 and 2 × 3.0 Hz; 1-H), 2.22 (s; CH_3), 2.12 (s; 2 CH_3), 2.12 (m; 3-eq-H), 1.99 (m; 6-ax-H), 1.85 (m; 6-eq-H), 1.85, 1.53, 1.40 and 1.32 (4-CH_2 and 5-CH_2), 1.32 (m; 3-ax-H).

^{13}C NMR ($CDCl_3$): δ = 210.7 (C=O), 156.9 (*ipso*-phenyl-C), 138.1 and 138.0 (1- and 4-mesityl-C), 133.3 (2- and 6-mesityl-C), 129.3 (2 *m*-phenyl-C), 128.5 (3- and 5-mesityl-C), 120.8 (*p*-phenyl-C), 116.4 (2 *o*-phenyl-C), 71.7 (C-2), 54.5 (C-1), 28.1 (C-3), 22.1 (C-6), 25.3 and 19.7 (4-CH_2 and 5-CH_2), 21.0 (CH_3), 19.4 (2 CH_3).

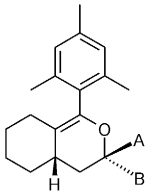
18: ^{1}H NMR ($CDCl_3$): δ = 7.19 (6-phenyl-H), 7.07 (4-phenyl-H), 6.93 (3-phenyl-H), 6.87 (5-phenyl-H), 6.72 (s; 3- and 5-mesityl-H), 3.26 (td; J = 2 × 10.6 and 3.0 Hz; 2-H), 3.09 (td; J = 2 × 10.6 and 3.4 Hz; 1-H), 2.21 (s; CH_3), 1.99 (m; 6-eq-H), 1.88 (s; 2 CH_3), ∼1.86 (m; 3-eq-, 4-eq- and 5-eq-H), 1.74 (m; 3-ax-H), ∼1.33 (m; 4-ax-, 5-ax- and 6-ax-H).

^{13}C NMR ($CDCl_3$): $\delta = 215.2$ (C=O), 153.7 (2-phenyl-C), 139.1, 134.3 and 132.2 (3 *ar*-C), 136.9 (2- and 6-mesityl-C), 128.8 (3- and 5-mesityl-C), 127.6 and 127.5 (4- and 6-phenyl-C), 120.9 (5-phenyl-C), 118.8 (3-phenyl-C), 59.5 (C-1), 35.3 (C-2), 32.2 (C-3), 30.7 (C-6), 26.2 (C-4 and -5), 21.0 (CH_3), 19.6 (2 CH_3).

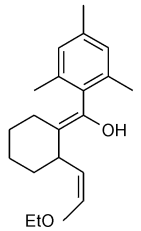
3. Results

3.1. Irradiation of 8 in ethyl vinyl ether

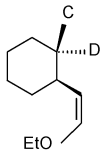
This reaction, carried out in exact analogy to **1**, gave a quite analogous result [3]. The two stereoisomers **11a** and **11b** were obtained in a ratio of 3:2 and a combined yield of 61.5% (isolated yield 56%), based on unrecovered **8**. This result, in analogy to **1** [3], demonstrates the intermediate formation of **9**. Besides **11a** and **b**, 11.5% of the kinetically stable enol **12** can be detected in the ^{1}H NMR spectrum of the crude product after evaporation of the solvent (two olefinic H at $\delta = 4.90$ (dd; $J = 9$ and 6 Hz) and 5.96 (dd; $J = 6$ and 1.3 Hz) and one OH at $\delta = 6.20$ (s; selectively removed upon shaking the $CDCl_3$ solution with D_2O and measured immediately thereafter)). **12** is unstable to moisture and air; on chromatography it is converted to a 2:1 mixture of **13a** and **13b**, neither of which is present in the original reaction product. The two *E* isomers of **13a** and **b** are also obtained from this chromatography at a combined yield of 1%. The strong predominance (ca. 10:1) of *Z*-configurated olefinic double bonds in these products points to the following mechanism for the formation of **12**: a conformationally equilibrated (and hence, rather long lived) enolate/alkoxycarbenium zwitterion is an intermediate which can possess two conformations suitable for intramolecular H-abstraction by the enolate oxygen. For electrostatic reasons, the one with the closer distance between the two oppositely charged oxygen atoms (see molecular models, Scheme 3) is preferred.



11	A	B
a	OEt	H
b	H	OEt

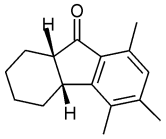


12

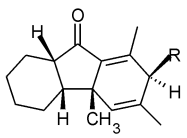


13	C	D
a	mesitoyl	H
b	H	mesitoyl

Scheme 3.



14



15	R
a	OH
b	$OCOCH_3$
c	H

Scheme 4.

3.2. Irradiation of 8 in the presence of acetic acid

The irradiation of **8** in acetonitrile containing 10% acetic acid gave a result entirely different from that obtained in acetonitrile alone. In place of a complex mixture, **14** was obtained as the main product. The route to **14**, which is a trimethyl derivative of **5**, is obviously similar to that of **5** in acidic media: protonation of the basic oxygen atom in **10** may trigger a Wagner–Meerwein 1,2-migration of the tertiary methyl group, followed by a deprotonation that regenerates the aromatic system to give the enol of **14**. The formation of **14** thus is an evidence for intermediate **10**. **15a** and **b**, formed as minor products besides **14**, even more clearly reveal their origin from **10** and verify the stereochemistry of the ring-closure reaction **9** → **10** to be the same as in **2** → **3** (Scheme 4).

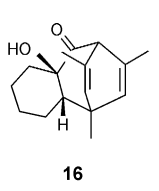
The crude irradiation mixture, after removal of the acetic acid by washing with aqueous sodium bicarbonate, showed in its ^{1}H NMR spectrum the presence of one further, unidentified, product (triplet at $\delta = 3.14$) in one fourth the amount of **14**. This product did neither survive extraction with aqueous sodium hydroxide nor distillation below 100°C nor chromatography. Rather, chromatography of the crude mixture reproducibly yielded two zones each of **14** and of **15a**, the second zone of **14** being much minor to the first one, which indicates that the unidentified product is converted to **14** and **15a** on the column.

3.3. Irradiation of 8 in the presence of water

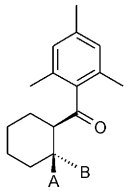
The irradiation of **8** in a 2:1 (v/v) mixture of acetonitrile and water led mostly to polymer. Only 9.4% monomeric material was recovered from chromatography; this consists of unchanged **8** (3.8%), **14** (0.5%), and the new substances **15c** (0.3%) and **16** (3.9%). A possible mechanism for the formation of **16** is the addition of water across the oxyallyl moiety of **10**, followed by an all-suprafacial photochemical [1,3]acyl migration.

3.4. Irradiation of 8 in the presence of phenol

The idea behind this experiment was to exploit the reaction principle exemplified by the surprisingly efficient addition of the enol **4** to the oxyallyl **3** to give **6** (see Scheme 1) [2]. Phenol might conceivably assume the role of **4**. When applied to **3** this idea had failed; rather, phenol or the acidic



16



	A	B
17	phenoxy	H
18	H	2-hydroxyphenyl

Scheme 5.

enol dimedone catalysed the prototropic reaction **3** → **4**. **10**, which does not so readily undergo a corresponding rearrangement (vide supra), was hoped to stand a better chance in this respect. In the event, however, the irradiation of **8** in the presence of a large excess of phenol (10% in acetonitrile) to ca. 60% conversion gave (based on unrecovered **8**) the phenol adducts **17** (8.6%) and **18** (8.1%), and furthermore **14** (1.2%), **15a** (4.2%), **15c** (2.1%), and numerous further minor products which could not be separated and the molecular structures of which could not be ascertained. It is evident that the targeted reaction principle does not prevail in this case (Scheme 5).

15c is the adduct of two hydrogen atoms of **10**. It reflects the ability of phenol to donate both single electrons and protons, and thus to hydrogenate strong electrophiles. Ascorbic acid is known to be an even better donor of electrons and protons; therefore, the irradiation of **8** in the presence of ascorbic acid (14% ascorbic acid in 2:1 acetonitrile/water or in 2:1 acetonitrile/dimethyl sulphoxide) was attempted in the hope of producing higher yields of **15c**. However, very complicated reaction mixtures were obtained which we did not separate.

4. Conclusion

The photolysis of **8** in the presence of selected additives demonstrated that **8**, in analogy to **1**, on irradiation is converted to intermediates **9** and **10**. Of the photoreactions of **8** investigated, the conversion to **14** in the presence of acid and the formation of [4 + 2] adducts in enol ethers hold synthetic promise. Products **15a–c** and **16** are novel and have no precedent in the photochemistry of **1**.

Acknowledgements

The authors wish to thank Mr. Jörg Bitter and Mrs. Kerstin Sand for carrying out the NMR experiments. AEMG gratefully acknowledges the grant from DAAD (Deutscher Akademischer Austauschdienst).

References

[1] A.B. Smith III, W.C. Agosta, J. Am. Chem. Soc. 95 (1973) 1961.
[2] J. Leitich, I. Heise, S. Werner, C. Krüger, K. Schaffner, J. Photochem. Photobiol. A 57 (1991) 127.
[3] A.E.-A.M. Gaber, I. Heise, J. Leitich, K. Schaffner, J. Photochem. Photobiol. A 123 (1999) 31.
[4] I.L. Kondakov, Bull. Soc. Chim. Fr. 7 (1892) 576.
[5] J. Graefe, M. Mühlstädt, D.M. Müller, Tetrahedron 26 (1970) 2677.
[6] E. Klein, W. Rojahn, Tetrahedron Lett. (1971) 3607.
[7] W. Rojahn, E. Klein, Dragoco Report, 1979, p. 103.
[8] R.P. Barnes, Org. Synth. 21 (1941) 77.