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The photo-Nazarov cyclisation of 1-cyclohexenyl-phenyl-methanone revisited II: Reaction between primary and secondary key intermediates

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Abstract

Trans-1-cyclohexenyl-phenyl-methanone (**2**) and enol **4**, both key intermediates in the title reaction, react with each other in a Michael-type addition to form predominantly enol **10**. This enol, kinetically stable but too reactive to be isolated, reveals its presence in the irradiated solutions by formation of the isomeric ketone **11** on acid catalysis, and by formation of the oxidation product **9** on exposure to atmospheric oxygen. In the absence of acid, formation of **10** competes significantly with the title reaction of *cis*-1-cyclohexenyl-phenyl-methanone (**1**). In a secondary photoreaction of **10**, 1,6-hydrogen abstraction by the excited carbonyl group and cyclisation afford **13** and **14**. Enols **4**, **10**, and **13**, in striking contrast to enol ethers and to thermodynamically stable enols, are unstable towards atmospheric oxygen. Thus, **4** autoxidises to form five compounds (**Ox**-1 through **Ox**-5), **10** to form **9**, and **13** to form **15**.

Keywords: Nazarov cyclisation; *Trans*-1-cyclohexenyl phenyl ketone; Enols; Michael addition; Autoxidation

1. Introduction

The near-UV irradiation of 1-cyclohexenyl-phenyl-methanone (**1**) to give the hexahydrofluorenone **5** has been known for about 27 years as the "photo-Nazarov reaction" [1]. Some years ago, we established the mechanism of this reaction as shown in Scheme 1 [2]. When conducted in the presence of catalytic amounts of acid, the formation of **5** from **1** is quite clean and, thus, holds promise as a prototype for a more general synthetic method. In the absence of acid in non-protic solvents such as acetonitrile, however, high yields of **6** can be isolated, and several other minor by-products form as well. The most important action of the added acid is to convert the enols **4** and **6**, which are kinetically stable in the absence of acid, to the ketones **5** and **7**, respectively; **7** is further converted to **5** under the irradiation conditions (Scheme 1) [2]. We now report further reactions that occur upon irradiation of **1** in the absence of acid in acetonitrile, and the starting point of which is again enol **4**. The share of these reactions is expected to increase with the lifetime of **4** under the irradiation conditions, and this lifetime depends on adventitious catalysis which converts **4** to **5** and which is difficult to control experimentally. Thus, the extent of this reaction (i.e. the sum of the yields of all its secondary products) in the absence of catalytic amounts of acid in acetonitrile was mostly 6–15%, but in one run it was found to be as high as 42%.

2. Experimental

2.1. General aspects

Unless specified otherwise, experiments were carried out as described previously [2].

A preparative irradiation of **1** in acetonitrile under an argon atmosphere was carried out and worked up immediately after irradiation as described. After separation of **6** by crystallisation, chromatography of the residue on silica gel 0.04–0.063 mm (Merck) with dichloromethane gave **7**, **1**, **5**, fraction four, fraction five, **16**, fraction seven, hydroxy-**7** [2], fraction nine, **Ox**-1, **Ox**-2, in this sequence. Products **7**, **1**, **5**, and hydroxy-**7** [2] were the main constituents. **Ox**-1 through **Ox**-5 were products formed by reaction of **4** with atmospheric oxygen: *cis*-9a-hydroxy- 1,2,3,4,4a,9a-hexahydrofluoren-9-one (**Ox-**1) [3], *cis*- and *trans*- 1,2,3,4,4a,10b-hexahydro-10b-hydroxy-benzo[*c*] chromen-6-one (**Ox**-2), *cis*-1,2,3,4,4a,10b-hexahydro-benzo[*c*]chromen-6-one (**Ox**-3) [4], *trans*-1,2,3,4,4a, 10b-hexahydro-benzo[*c*]chromen-6-one (**Ox**-4) [4], and

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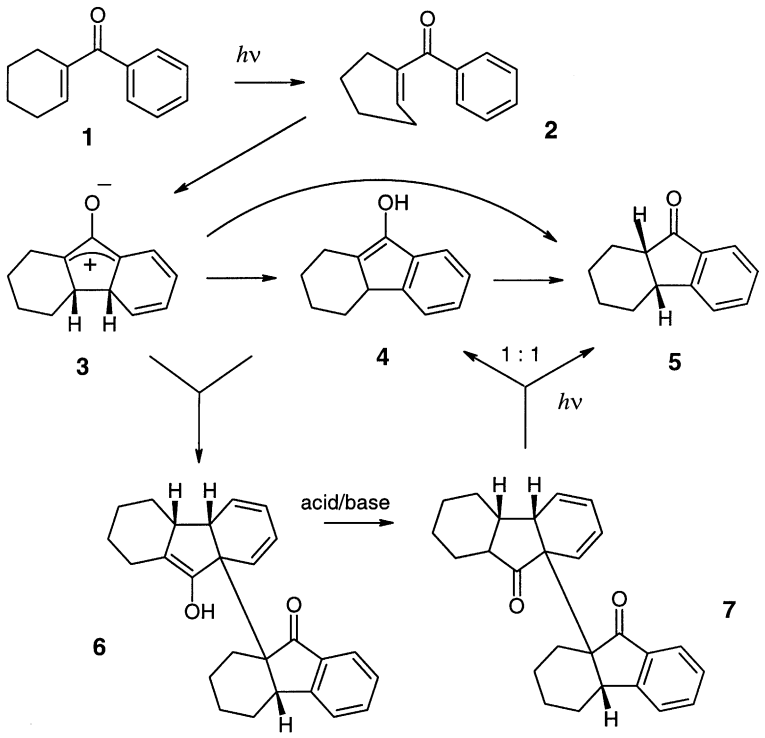


Scheme 1. Mechanism of photo-Nazarov reaction.

1,2,3,4-tetrahydro-benzo[*c*]chromen-6-one (**Ox**-5) [5]. Careful re-chromatography of the fractions eluted after **5** with *n*-hexane and 0–50% (gradually increasing) ether afforded, in the sequence given, from fraction four: **5**, epoxy-**1** [6], **Ox**-3, **Ox**-4; from fraction five: **5**, epoxy-**1**, **12**; from fraction seven: **Ox**-5, **16**, **8**, **14**, **9**, **17**; from fraction nine: hydroxy-**7** [2], **15**.

Another preparative experiment was carried out which differed from the former in that 10 mg *p*-toluene sulphonic acid per 50 ml of solution were added after irradiation without removing the argon atmosphere. After standing at room temperature for 10 h work-up and chromatography on silica gel 0.04–0.063 mm (Merck) with *n*-pentane+2% ether gave, in this sequence, **1**, **7**, **5**, **11**, **12**, **16**, **14**, **17**. Compounds **1**, **7**, **5** and **11** were the main constituents.

NMR experiments: Bruker DRX 400 instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

2.2. Elucidation of molecular structures

The unambiguous assignment of all molecular structures including the complete relative configurations was possible solely from NMR experiments with the exception of one chemical experiment which transformed **11** to **12** on base catalysis. NMR experiments encompassed 400 MHz ^{1}H-NMR including spin–spin decoupling and nuclear overhauser effect (NOE) experiments where profitable, 100 MHz ^{13}C-NMR, both broad band (BB decoupled from protons) and distortionless enhanced polarisation transfer (DEPT), and 400 MHz C, H correlation. Moreover, characteristic $J_{H,H}$ values as well as (e.g. in the cases of **11**, **14** and **8**) spectacular upfield shifts of aryl protons were very welcome for structural and stereochemical assignments.

2.3. *(4aR*,9aR*,1′S*,2′R*)-9a-(2-benzoyl-cyclohexyl)-4a,2′-epoxy-1,2,3,4,4a,9a-hexahydro-fluoren-9-one (***8***)*

From ether/pentane: mp 146°C. CI–MS: $m/z = 386$ (M^{+}).

^{1}H-NMR ($CDCl_3$): δ=7.60 (dd; $J = 8$ and 1.3 Hz; two *o*-phenyl-H), 7.52 (dt; $J = 7.7$ and 2×1 Hz; 8-H), 7.26 (tt; $J = 2 \times 8$ and 2×1.3 Hz; *p*-phenyl-H), 7.13 (ddd; $J = 7.7$, 7, and 1 Hz; 7-H), 7.09 (t; $J = 2 \times 8$ Hz; 2 *m*-phenyl-H), 6.99 (dt; $J = 7.7$ and 2×1 Hz; 5-H), 6.94 (ddd; $J = 7.7$, 7, and 1 Hz; 6-H), 2.61 (dtd; $J = 13.4$, 2×13.0, and 4.5 Hz; one 6′-H), 2.34 (dt; $J = 12.4$ and 2×3.4 Hz; one 3′-H), 2.06 (quasi-dd; $J = 5.7$ and 7.6 Hz; two 4-H), 2.03 (m; one 1-H), 1.99 (dm; $J = 13$ and $3 \times$ ca. 4 Hz; one 6′-H), 1.87 (dm; $J = 13.3$ and $3 \times$ ca. 4 Hz; one 5′-H), 1.86 (dd; $J =$ 13.4 and 3.8 Hz; 1′-H), 1.73 (ddd; $J = 13$, 12.4, and 4 Hz; one 3′-H), 1.69 (m; one 1-H), 1.66 (m; one 3-H), 1.58 (dm; $J = 13$ and $3 \times$ ca. 4 Hz; one 4′-H), 1.53 (tt; $J = 2 \times 10.9$ and 2×5.9 Hz; one 2-H), 1.29 (tdt; $J = 2 \times 13.3$, 12.5, and 2×4.3 Hz; one 5′-H), 1.08 (qd; $J = 3 \times 13.5$ and 2×4.0 Hz; one 4′-H), 1.02–1.16 (m; one 3-H, one 4-H).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): *o*-phenyl-H/5-H, *o*-phenyl-H/3′-H at 2.34, *m*-phenyl-H/5-H, 5-H/4-H, 6′-H at 2.61/4′-H at 1.08.

^{13}C-NMR ($CDCl_3$): δ, 206.6 (C-9), 201.7 (benzoyl-C=O), 152.4, 138.6, 134.9 (C-4b, C-8a, *ipso*-phenyl-C), 134.1 (C-6), 131.7 (*p*-phenyl-C), 129.4 (two *o*-phenyl-C), 129.3 (C-7), 127.1 (two *m*-phenyl-C), 125.4 (C-5), 122.2 (C-8), 88.7, 85.9 (C-4a, C-2′), 59.8 (C-1′), 57.0 (C-9a), 36.8 (C-3′), 29.8 (C-4), 28.3 (C-1), 25.9 (C-5′), 22.5 (C-6′), 21.7 (C-4′), 16.1 (C-2), 15.8 (C-3).

The (1′*R**) epimer was ruled out for two reasons: (1) the absence of ^{1}H, ^{1}H-NOE enhancements between 6′-H at 2.61 and protons on the opposite cyclohexane ring. For the (1′*R**) epimer strong enhancements would be expected because of very short internuclear distances; (2) the remarkably strong downfield chemical shift of the axial 6′-H at 2.61 is only explicable by a 1,3 diaxial interaction with the carbonyl edge of the benzoyl group. In the (1′*R**) epimer 1′-H would have exhibited this shift in place of the axial 6′-H; the observed shift for 1′-H (1.86), however, is normal.

2.4. (4aS*,9S*, 9aS*,1′R*, 2′R*)-(9a-cyclohexyl-9, 2′-epidioxy-9-hydroxy-2,3,4,4a,9,9a-hexahydro-1H-fluoren-2′-yl)-phenyl-methanone (**9**)

From ether/pentane: mp 154–159°C. CI–MS: $m/z = 404$ (M^+). Found: C 77.20, H 6.80; $C_{26}H_{28}O_4$ requires C 77.20, H 6.98.

^{1}H-NMR ($CDCl_3$): δ = 8.13 (dd; J = 7.7 and 1.5 Hz; two *o*-phenyl-H), 7.41 (tt; $J = 2 \times 7.7$ and 2×1.5 Hz; one *p*-phenyl-H), 7.37 (dd; J = 7.5 and 0.8 Hz; 8-H), 7.31 (t; $J = 2 \times 7.7$ Hz; two *m*-phenyl-H), 7.28 (td; $J = 2 \times 7.5$ and 1.4 Hz; 6-H), 7.15 (tt; $J = 2 \times 7.5$ and 2×1.1 Hz; 7-H), 7.12 (bd; J = 7.5 Hz; 5-H), 3.72 (variable; one OH), 3.71 (dd; J = 4.3 and 3 Hz; 4a-H), 2.77 (tdd; $J = 2 \times 13.7$, 12, and 4.3 Hz; one 6′-H), 2.24 (dd; J = 13.7 and 3.5 Hz; 1′-H), 2.23 (m; one 6′-H), 2.22 (m; one 4-H), 2.11 (dtd; J = 12.5, 2×3.0, and 1.3 Hz; one 3′-H), 1.94 (tdd; $J = 2 \times 14$, 4.3, and 3.8 Hz; one 4-H), 1.60 (ddd; J = 13, 12.5, and 4 Hz; one 3′-H), 1.96/1.45 (two 5′-H), 1.69/1.39 (two 4′-H), 1.60/1.45 (two 2-H), 1.50/1.42 (two 1-H), 1.45 (m; one 3-H), 1.06 (dtt; $J = 14$, 2×13, and 2×4 Hz; one 3-H).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): 4a-H/*o*-phenyl-H, *o*-phenyl-H/3′-H at 2.11, *o*-phenyl-H/OH, OH/6′-H at 2.77, 6′-H at 2.77/4a-H.

^{13}C-NMR ($CDCl_3$): δ= 202.5 (C=O), 146.8 (*ipso*-phenyl-C), 137.4, 136.6 (C-4b and C-8a), 132.3 (*p*-phenyl-C), 130.2 (C-6), 129.6 (two *o*-phenyl-C), 128.1 (two *m*-phenyl-C), 126.3 (C-7), 124.2 (C-8), 123.3 (C-5), 111.8 (C-9), 89.3 (C-2′), 54.0 (C-1′), 47.5 (C-9a), 41.3 (C-4a), 34.0 (C-3′), 31.7 (C-1), 26.8 (C-5′), 26.2 (C-6′), 24.5 (C-2), 24.2 (C-4), 21.6 (C-4′), 19.4 (C-3).

2.5. (4aS*,9aR*,1′S*,2′R*)-9a-(2-benzoyl-cyclohexyl)-1,2, 3,4,4a,9a-hexahydro-fluoren-9-one (**11**)

Mp 113–115°C. EI–MS: 372 (M^+). Found C 83.73, H 7.71; $C_{26}H_{28}O_2$ (372.5) requires C 83.83, H 7.58.

^{1}H-NMR ($CDCl_3$): δ= 7.35 (d; J = 7.8 Hz; two *o*-phenyl-H), 7.30 (d; J = 7.8 Hz; 8-H), 7.25 and 7.23 (m; 6-H and 7-H), 7.21 (m; 5-H), 7.11 (t; $J = 2 \times 7.7$ Hz; two *m*-phenyl-H), 6.87 (t; $J = 2 \times 7.6$ Hz; *p*-phenyl-H), 3.74 (dd; J = 5.2 and 3.4 Hz; 4a-H), 3.71 (td; $J = 2 \times 4.0$ and 3.6 Hz; 2′-H), 2.42 (dtd; J = 13.1, 2×12.5, and 3.8 Hz; one 6′-H), 1.95 (dt; J = 13.1 and 2×3.5 Hz; 1′-H), 1.80 (dq; J = 12.7 and 3×3.4 Hz; one 6′-H), 1.93/1.32, 1.92/1.72, 1.88/1.68, 1.61/1.41, 1.61/1.41, 1.41/1.02, 1.28/0.84 (seven CH_2).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): 2′-H/*o*-phenyl-H, 8-H/*m*-phenyl-H, 8-H/*p*-phenyl-H, 4a-H/6′-H at 2.42.

^{13}C-NMR ($CDCl_3$): δ= 213.4 (C-9), 202.8 (benzoyl-C=O), 158.6, 137.1, 137.0 (C-4b, C-8a, and *ipso*-phenyl-C), 134.8, 131.9 (C-6 and C-7), 127.9 (two *m*-phenyl-C), 127.3 (two *o*-phenyl-C), 127.0 (*p*-phenyl-C), 125.4 (C-5), 122.9 (C-8), 56.4 (C-9a), 48.5 (C-1′), 40.6, 40.4 (C-4a and C-2′), 30.5, 29.6, 26.9, 25.7 (four CH_2), 23.0 (C-6′), 20.7, 18.1, 16.3 (three CH_2).

2.6. (4aS*,9aR*,1′S*,2′S*)-9a-(2-benzoyl-cyclohexyl)-1,2,3, 4,4a,9a-hexahydro-fluoren-9-one (**12**)

MS: $m/z = 372$ (M^+).

^{1}H-NMR ($CDCl_3$): δ= 8.18 (d; J = 7.5 Hz; two *o*-phenyl-H), 7.64 (d; J = 7.6 Hz; 8-H), 7.55 (td; $J = 2 \times 7.5$ and 1.1 Hz; *p*-phenyl-H), 7.53 (tt; J = 7.7, 7.2, and 2×1.3 Hz; 6-H), 7.48 (t; $J = 2 \times 7.5$ Hz; two *m*-phenyl-H), 7.43 (d; J = 7.7 Hz; 5-H), 7.31 (t; J = 7.6 and 7.2 Hz; 7-H), 4.15 (ddd; J = 10.9, 10.3, and 3.8 Hz; 2′-H), 3.38 (dd; J = 5.2 and 3.5 Hz; 4a-H), 2.42 (ddd; J = 12.4, 10.3, and 3.6 Hz; 1′-H), 1.98 (ddt; J = 14, 12, and 2×5.2 Hz; one 4-H), 1.84 (ddt; J = 14, 5.1, and 2×3.5 Hz; one 4-H), 1.83/1.19 (two m; two 3′-H), 1.68 (m, coupled to 1′H by 3.6 Hz; one 6′-H), 1.46 (ddd; 13.4, 10.7, and 4.5 Hz; one 1-H), 1.39 (dt; J = 13.4 and 2×4.9 Hz; one 1-H), 0.90 (m, coupled to 1′-H by 12.4 Hz; one 6′-H), 1.63/1.19, 1.61/1.19, 1.30/0.91, 1.28/0.80 (four CH_2).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): 4a-H/1′-H, 4a-H/6′-H at 1.68, 1′-H/1-H at 1.46, 2′-H/*o*-phenyl-H.

^{13}C-NMR ($CDCl_3$): δ=212.6 (C-9), 204.8 (benzoyl-C=O), 157.5, 137.8, 136.9 (C-4b, C-8a, and *ipso*-phenyl-C), 134.7 (*p*-phenyl-C), 132.7 (C-6), 128.7 (two *o*-phenyl-C), 128.6 (two *m*-phenyl-C), 127.4 (C-7), 124.9 (C-5), 123.0 (C-8), 56.3 (C-9a), 44.8 (C-2′), 44.6 (C-4a), 44.1 (C-1′), 32.8 (C-3′), 29.7 (C-1), 27.2 (C-6′), 25.9, 25.6 (2 CH_2), 24.4 (C-4), 17.9, 17.2 (two CH_2).

2.7. (4aR*,4bS*,8aS*,12bS*,13S*)-2,3,4,4a,6,7,8,8a, 12b,13-decahydro-13-phenyl-5H-indeno[1,2-k]-fluorene-12b,13-diol (**14**)

From ether/pentane: mp 189°C; EI–MS and CI–MS: $m/z = 372$ (M^+).

In its NMR spectra, the compound shows hindered rotation of its phenyl group: At 233 K all five phenyl protons

are non-equivalent. At room temperature. two pairs of signals belonging to the *o*-phenyl and *m*-phenyl protons have merged to form one broad signal which sharpens at 300 K. The analogous phenomenon is exhibited by the ^{13}C resonances. These phenomena are reversible.

^{1}H-NMR ($CDCl_3$, 300 K): δ=7.0 (m; split into two equal d (7.8 Hz) at 7.70 and 6.23 at 213 K; two *o*-phenyl-H), 7.0 (m; split into two equal t (7.4 Hz) at 7. 23 and 6.70 at 213 K; two *m*-phenyl-H), 7.0 (m; *p*-phenyl-H), 6.97 (m; 9-H, 10-H), 6.70 (bdd; J = 7.5 and 6 Hz; 11-H), 6.40 (d; J = 7.5 Hz; 12-H), 5.61 (dtd; J = 4.8, 2 × 2.5, and 0.8 Hz; 1-H), 4.01 (variable s; OH), 3.08 (variable s; OH), 3.04 (ddt; J = 5.7, 2, and 2 × 0.5 Hz; 8a-H), 2.93 (dddt; J = 13, 4.6, 3, and 2 × 2.5 Hz; 4a-H), 2.27 (dddd; J = 13.1, 5, 4.5, and 2.5 Hz; one 4-H), 2.24 (ddq; J = 13.9, 4.6, and 3 × 2.0 Hz; one 8-H), 2.10 (ddddd; J = 18, 10.8, 5, 4.6, and 2.5 Hz; one 2-H), 2.01 (d, J = 18 Hz, of a m, 12 Hz wide; one 2-H), 1.91 (dddtd; J = 12, 5, 4.5, 2 × 2.5, and 0.8 Hz; one 3-H), 1.81 (tdd; J = 2 × 13.9, 5.7, and 0.5 Hz; one 8-H), 1.70 (d, J = 13 Hz, of a m, 9 Hz wide; one 5-H), 1.65 (tdd; J = 13.1, 13, 11, and 2.5 Hz; one 4-H), 1.54-1.60 (m; 4 H; 3-H, 5-H, 6-H, 7-H, one each), 1.46 (m; one 6-H), 1.06 (q, J = 3 × 13 Hz, of a m; one 6-H).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): phenyl-H/OH at 4.01, 12-H/OH at 3.08, 4-H at 1.65/8-H at 1.81, 4-H at 1.65/8a-H.

^{13}C-NMR ($CDCl_3$, 323 K): δ=149.5, 145.3, 143.9, 141.9 (C-8b, C-12a, C-13a, and *ipso*-phenyl-C), 127.5, 126.2, 121.5 (C-9, C-10, and *p*-phenyl-C), 127.1 (split into two equal resonances at 127.4 and 126.0 at 233 K; two *o*-phenyl-C), 126.6 (split into two equal resonances at 127.1 and 125.8 at 233 K; two *m*-phenyl-C), 126.1 (C-11), 125.3 (C-12), 124.3 (C-1), 95.9, 83.5 (C-12b, C-13), 59.3 (C-4b), 47.7 (C-4a), 42.0 (C-8a), 30.2 (C-5), 27.1 (C-4), 25.6 (C-8), 25.1 (C-2), 22.9 (C-6), 22.7 (C-3), 20.8 (C-7).

2.8. (4aS,5R*,6S*,7R*,7aS*,11bS*)-6-benzoyl-6-hydroxy-1,2,3,5,6,7,7a,11b-octahydro-5,7-propano-4H-cyclopentano[k]fluoren-7a-ol (***15***)*

From ether: mp 219–222°C. ESIpos–MS: m/z = 388 (M^+). Found: C 80.00, H 7.33; $C_{26}H_{28}O_3$ (388.5) requires C 80.38, H 7.26.

^{1}H-NMR ($CDCl_3$): δ=8.09 (bd; J = 7.6 Hz; two *o*-phenyl-H), 7.51 (tt; J = 2 × 7.4 and 2 × 1.3 Hz; *p*-phenyl-H), 7.43 (t; J = 2 × 7.5 Hz; two *m*-phenyl-H), 7.36 (dd; J = 6.9 and 2 Hz; 8-H), 7.29 (td; J = 2 × 7 and 2 Hz; 10-H), 7.27 (td; J = 2 × 7 and 1.6 Hz; 9-H), 7.16 (bd; J = 7 Hz; 11-H), 4.36 (variable s; 6-OH), 3.38 (dd; J = 11 and 6 Hz; 11b-H), 2.91 (variable s; 7a-OH), 2.86 (td; J = 2 × 4 and 3.5 Hz; 7-H), 2.80 (dt; J = 4 and 2 × 2.5 Hz; 5-H), 2.15 (quasi-q; J = 3 × 4.0 Hz; one 4-H), 2.04 (dddd; J = 12.5, 6, 4, and 3 Hz; one 1-H), 1.92 (dddd; J = 14.5, 12, 8, and 4 Hz; one 3′-H), 1-70-1.74 (m; one 2-H, two 3-H, one 4-H, one 1′-H), 1.60 (dddd; J = 15.5, 12.5, 7.5, and 2.5 Hz; one 1′-H), 1.46 (tdd; J = 2 × 12.5, 11, and 3.5 Hz; one 1-H), 1.31 (m; one 2-H), 1.17 (dddd; J = 14.5, 8, 3.5, and 1 Hz; one 3′-H), 0.85 (dtt; J = 13.5, 2 × 8.0, and 2 × 1.0 Hz; one 2′-H), 0.72 (ddddd; J = 13.5, 12, 11.5, 8, and 7.5 Hz; one 2′-H).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): 1-H at 2.04/11H, 5-H/*o*-phenyl-H, 5-H/6-OH, 5-H/4-H at 2.15, 4-H at 2.15/6-OH, 5-H/11b-H, 11b-H/2-H at 1.31, 11b-H/11-H, 11b-H/1′-H at 1.74, 11b-H/2′-H at 0.72, 7-H/*o*-phenyl-H, 7-H/6-OH, 7-H/8-H, 6-OH/*o*-phenyl-H.

^{13}C-NMR ($CDCl_3$): δ=198.5 (C=O), 148.6, 141.9, 137.5 (C-7b, C-11a, and *ipso*-phenyl-C), 132.1 (*p*-phenyl-C), 129.1 (3 CH; C-10, two *o*-phenyl-C), 128.2 (two *m*-phenyl-C), 127.2 (C-9), 125.4 (C-8), 123.8 (C-11), 96.7, 92.1 (C-6, C-7a), 57.3 (C-4a), 54.3 (C-7), 48.8 (C-5), 44.9 (C-11b), 26.7 (C-4), 25.9 (C-1), 25.5 (C-1′), 24.7 (C-3′), 19.0 (C-2), 18.0 (C-3), 14.6 (C-2′).

2.9. (4aR,5S*,6S*,7R*,7aS*,11bS*)-6-benzoyl-1,2,3,5,6,7,7a,11b-octahydro-5,7-propano-4H-cyclopentano[k]-fluoren-7a-ol (***16***)*

Insoluble in ether: mp 244°C. MS: m/z = 372 (M^+). Found: C 83.15, H 7.56; $C_{26}H_{28}O_2$ (372.5) requires C 83.83, H 7.58.

^{1}H-NMR ($CDCl_3$): δ=8.00 (dd; J = 8 and 1.3 Hz; two *o*-phenyl-H), 7.60 (tt; J = 2 × 7.4 and 2 × 1.3 Hz; *p*-phenyl-H), 7.49 (bdd; J = 8 and 7.4 Hz; two *m*-phenyl-H), 7.44 (m; 8-H), 7.25 (m; 9-H, 10-H), 7.10 (m; 11-H), 5.14 (variable s; OH), 3.44 (bs; 6-H), 3.16 (dd; J = 10.9 and 5.7 Hz; 11b-H), 3.03 (td; J = 2 × 3.7 and 2.3 Hz; 7-H), 2.78 (ddd; J = 3.6, 3, and 2.3 Hz; 5-H), 2.10 (ddd; J = 14.1, 6.9, and 3.6 Hz; one 1′-H), 1.94 (dddd; J = 14.1, 12.5, 7, and 3 Hz; one 1′-H), 1.88 (ddt; J = 14, 5.7, and 2 × 3.5 Hz; one 1-H), 1.66 (ddd; J = 14.4, 11.8, and 6 Hz; one 4-H), 1.60 (ddd; J = 14, 7.5, and 3.6 Hz; one 3′-H), 1.52 (m; one 2-H), 1.51 (dddd; J = 14, 12.5, 7, and 3.7 Hz; one 3′-H), 1.46 (m; one 3-H), 1.38 (dddd; J = 14, 11.6, 10.9, and 3.6 Hz; one 1-H), 1.20 (m; one 2-H), 1.14 (dt; J = 14.6 and 2 × 7.0 Hz; one 2′-H), 1.11 (m; one 3-H), 0.90 (dtdd; J = 14.6, 2 × 12.5, 7.5, and 6.9 Hz; one 2′-H), 0.85 (ddd; J = 14.4, 5.2, and 3 Hz; one 4-H).

^{1}H,^{1}H-NOE enhancements ($CDCl_3$): 4-H at 0.85/OH, 4-H at 0.85/5-H, 5-H/11b-H, 5-H/*o*-phenyl-H, 5-H/6-H, 6-H/*o*-phenyl-H, 6-H/7-H, 6-H/1′-H at 1.94, 6-H/3′-H at 1.51, 7-H/OH, 7-H/8-H, 8-H/3′-H at 1.60, 11-H/1-H at 1.88, 11-H/11b-H, 11b-H/1′-H at 2.10, 11b-H/2′-H at 0.90.

^{13}C-NMR ($CDCl_3$): δ=206.9 (C=O), 148.7 143.0, 135.5 (C-7b, C-11a, and *ipso*-phenyl-C), 133.5 (*p*-phenyl-C), 128.8 (two *o*-phenyl-C), 128.7 (two *m*-phenyl-C), 128.3, 126.8 (C-9, C-10), 125.8 (C-8), 123.1 (C-11), 96.0 (C-7a), 63.9 (C-6), 58.6 (C-4a), 50.0 (C-5), 47.8 (C-7), 44.3 (C-11b), 31.0 (C-1′), 30.3 (C-3′), 26.0 (C-1), 25.5 (C-4), 18.9 (C-2), 17.4 (C-3), 17.0 (C-2′).

2.10. (4aR,5S*,6R*, 7R*,7aS*,11bS*)- 6-benzoyl-1,2,3, 5,6,7,7a,11b-octahydro-5,7-propano-4H-cyclopentano[k] fluoren-7a-ol (***17***)*

From ether/pentane: mp 185–187°C. MS: $m/z = 372$ (M^+).

^{1}H-NMR ($CDCl_3$): δ=7.90 (bd; J = 7.4 Hz; two *o*-phenyl-H), 7.52 (tt; $J = 2 \times 7.3$ and 2×1.4 Hz; *p*-phenyl-H), 7.45 (tt; $J = 2 \times 7.4$ and 2×1.5 Hz; two *m*-phenyl-H), 7.34 (bd; J = 7.2 Hz; 8-H), 7.28 (td; $J = 2 \times 7.3$ and 1.5 Hz; 10-H), 7.24 (bt; $J = 2 \times 7.3$ Hz; 9-H), 7.18 (bd; J = 7.3 Hz; 11-H), 4.15 (tt; $J = 2 \times 4.4$ and 2×1.5 Hz; 6-H), 3.30 (dd; J = 10.8 and 6.1 Hz; 11b-H), 2.80 (dtd; J = 4.4, 2×3.5, and 2 Hz; 7-H), 2.58 (dddd; J = 4.4, 3.5, 3, and 2 Hz; 5-H), 2.05 (ddt; J = 12.5, 6.1, and 2×4 Hz; one 1-H), 1.98 (variable s; OH), 1.90 (dddd; J = 14, 13, 7.5, and 3 Hz; one 1′-H), 1.87 (dddd; J = 14, 12.6, 7.5, and 3.4 Hz; one 3′-H), 1.73 (m; one 3-H), 1.6-1.7 (m; one 2-H, one 3-H, two 4-H), 1.60 (dddd; J = 14, 7, 3.5, and 1.5 Hz; one 1′-H), 1.42 (m; one 1-H), 1.33 (m; one 2-H), 1.11 (dddt; J = 14, 7.3, 3.5, and 2×1.5 Hz; one 3′-H), 0.99 (dtd; J = 14, 2×7.5, and 1.5 Hz; one 2′-H), 0.74 (ddddd; J = 14, 13, 12.6, 7.3, and 7 Hz; one 2′-H).

^{1}H, ^{1}H-NOE enhancements ($CDCl_3$): 1-H at 2.05/11-H, 11-H/11b-H, 11b-H/5-H, 11b-H/1′-H at 1.60, 11b-H/2′-H at 0.74, 5-H/*o*-phenyl-H, *o*-phenyl-H/6-H, *o*-phenyl-H/7-H, 6-H/OH, 7-H/OH, OH/8-H, 8-H/7-H, 8-H/3′-H at 1.11.

^{13}C-NMR ($CDCl_3$): δ=203.2 (C=O), 149.1, 142.7, 138.5 (C-7b, C-11a, and *ipso*-phenyl-C), 132.3 (*p*-phenyl-C), 128.9 (C-10), 128.5 (two *m*-phenyl-C), 128.0 (two *o*-phenyl-C), 127.1 (C-9), 125.1 (C-8), 124.0 (C-11), 95.1 (C-7a), 57.2 (C-4a), 52.8 (C-6), 49.3 (C-7), 44.3 (C-5), 43.3 (C-11b), 26.2 (C-1), 25.1 (C-4), 22.7 (C-1′), 22.4 (C-3′), 19.0 (C-2), 18.2 (C-3), 16.3 (C-2′).

*2.11. Cis- and trans-1,2,3,4,4a,10b-hexahydro-4a-hydroxybenzo[c]chromen-6-one (**Ox**-2; two readily equilibrating stereoisomers, analysed as an 8:1 mixture)*

From ether: mp 158–168°C (dec.). MS: $m/z = 218$ (M^+). Found: C 70.84, H 6.32; $C_{13}H_{14}O_3$ (218.3) requires C 71.54, H 6.47.

2.11.1. Main isomer

^{1}H-NMR ($CDCl_3$): δ=8.07 (bd; J = 7.5 Hz; 7-H), 7.53 (bt; $J = 2 \times 7.5$ Hz; 9-H), 7.36 (tt; $J = 2 \times 7.5$ and 2×1 Hz; 8-H), 7.25 (bd; J = 7.5 Hz; 10-H), 4.1 (variable, OH), 2.91 (dd; J = 12 and 5 Hz; 10b-H), 2.24 (dt; J = 12 and 2×7 Hz; one 4-H), 1.93 (dq; J = 14 and 3×5 Hz; one 1-H), 1.76 (m; 2 H), 1.71 (ddd; J = 13, 12; and 3 Hz; one 4-H), 1.64 (m; 1 H), 1.38 (m; 1 H), 1.34 (dddd; J = 14, 13, 12, and 3 Hz; one 1-H).

^{13}C-NMR ($CDCl_3$): δ=165.6 (C-6), 143.1 (C-6a), 134.2 (C-9), 130.0 (C-7), 127.7 (C-10), 127.3 (C-8), 123.5 (C-10a), 102.5 (C-4a), 44.3 (C-10b), 37.7 (C-4), 33.8 (C-1), 24.3 (C-2), 22.6 (C-3).

2.11.2. Minor isomer

^{1}H-NMR ($CDCl_3$): δ=8.06 (bd; J = 7.5 Hz; 7-H), 7.58 (bt; $J = 2 \times 7.5$ Hz; 9-H), 7.37 (tt; $J = 2 \times 7.5$ and 2×1 Hz; 8-H), 7.30 (bd; J = 7.5 Hz; 10-H), 3.13 (dd; J = 12 and 4 Hz; 10b-H), 2.36 (dq; J = 14 and 3×4.0 Hz; one 1-H), 2.13 and 1.94 (2 m; two 4-H), 1.70 and 1.65 (m; two 3-H), 1.63 (dddd; J = 14, 13, 12, and 3 Hz; one 1-H), 1.49 (qt; $J = 3 \times 13.0$ and 2×4.0 Hz; one 2-H), 1.0 (m; one 2-H).

^{13}C-NMR ($CDCl_3$): δ=165.1 (C-6), 140.2 (C-6a), 134.0 (C-9), 129.9 (C-7), 127.1 (C-8), 125.4 (C-10a), 124.4 (C-10), 103.1 (C-4a), 43.2 (C-10b), 37.4 (C-4), 25.0 (C-2), 24.9 (C-1), 22.4 (C-3).

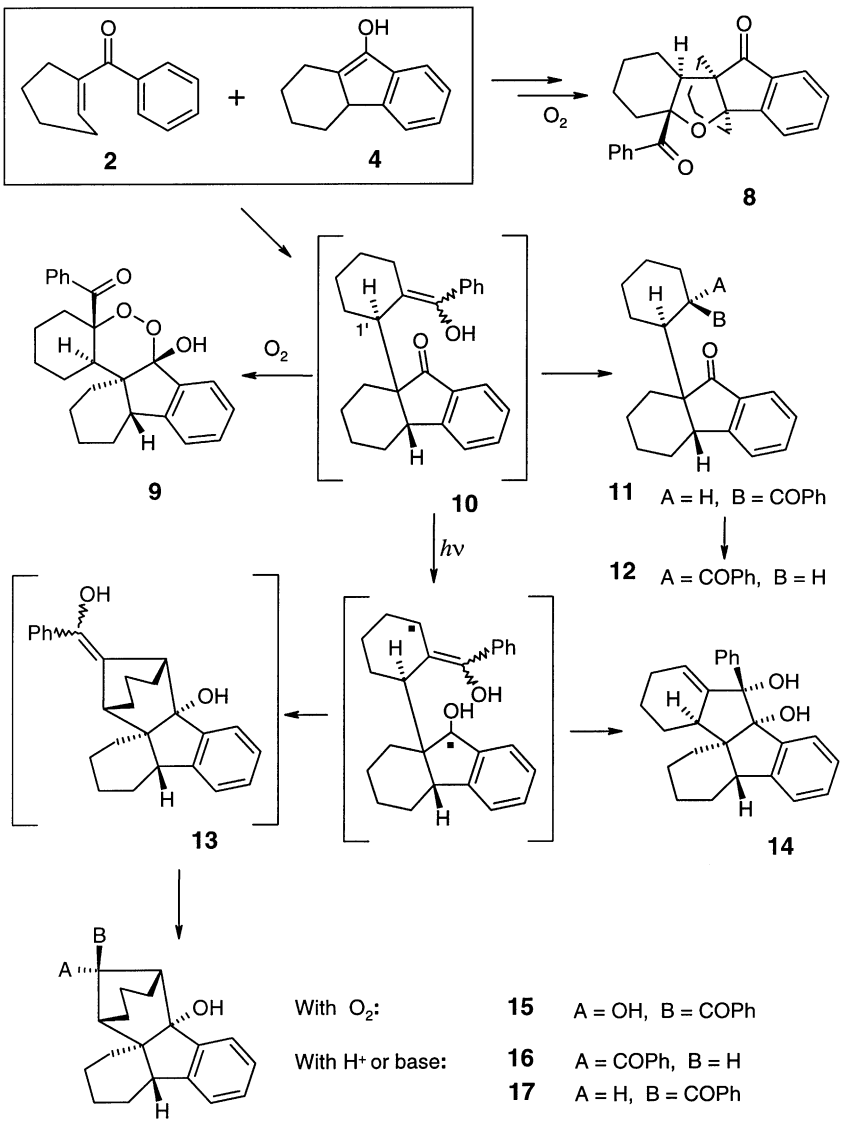
2.12. Epimerisation of **11**

A solution of 10 mg **11** in 1 ml freshly prepared 3 M sodium methoxide in methanol was left standing under an argon atmosphere at room temperature for 24 h. Work-up by distribution between ether and water and removal of solvent from the ether layer left a residue that was analysed by 400 MHz-^{1}H-NMR in $CDCl_3$ to be composed of 55% **11**, 35% **12**, and 10% unidentified material.

3. Results and discussion

When a catalytic amount of *p*-toluene sulphonic acid was added to a solution of **1** in acetonitrile after irradiation (>300 nm) under argon to a conversion of ca. 65%, and the acidified solution was left standing under argon for a few hours before work-up, then besides the known main products **5** and **7** [2] compounds **11**, **12**, **14**, **16**, and **17** were isolated (Scheme 2). We have shown before that acid rapidly converts products **4** to **5** and **6** to **7** [2]. When the acid treatment was omitted and work-up was carried out immediately after irradiation, then products **8**, **9**, and **15** were isolated at the expense of **11**, **12**, **14**, **16**, and **17**. The formation of all new compounds except **8** can be explained as outlined in Scheme 2. They arise from the enol intermediate **10** which obviously is kinetically stable under the irradiation conditions and is converted to **11** by the acid added after irradiation; **11**, in turn, can be converted to **12** by prolonged treatment with either acid or base. With atmospheric oxygen the intermediate **10** reacts rapidly to form **9**. Part of **10** photochemically forms **14** and the isomeric enol **13**. Similar to **10**, **13** is kinetically stable but is rapidly converted to its keto forms **16** and **17** by acid and to **15** by reaction with atmospheric oxygen. Formation of **16** and **17** from **11** or **12** under the irradiation conditions can be excluded since neither **11** nor **12** gave any **16** or **17** (400 MHz ^{1}H-NMR) when irradiated separately, but rather gave numerous other products that were not elucidated.

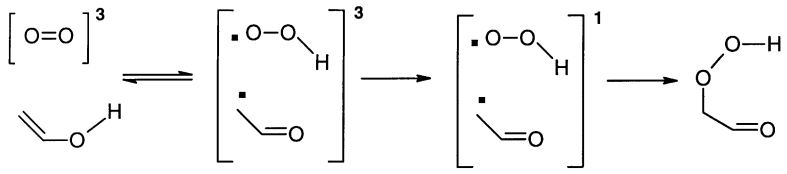
Product **8** obviously arises by the action of atmospheric oxygen on the C-1′ epimer of **10** which is formed in a small amount. One possible reaction sequence: the epimer of **10** with atmospheric oxygen forms a hydroperoxide analogous



Scheme 2. Formation of compounds **8**, **9**, **11**, **12**, **14**, **15**, **16**, and **17**.

to the open-chain (i.e. non-ketalised) form of **9**. The phenyl keto group in this compound can come into close contact to the benzylic hydrogen and on photoexcitation abstracts it to form a ketyl/benzyl diradical. The ketyl radical reduces the neighbouring hydroperoxy group, regenerating the phenyl ketone and cleaving the hydroperoxy group to water and oxyl radical. The oxyl and benzyl radicals then combine to form **8**.

The formation of **13** involves an intramolecular 1,6-hydrogen abstraction by the photo-excited carbonyl group of **10**. This 1,6-hydrogen abstraction prevails over the usually preferred 1,5-hydrogen abstraction (Norrish-type II)



Scheme 3. Oxidation of the kinetically stable enols by atmospheric oxygen.

even though it requires an axial position of the hexahydrofluorenone residue on the cyclohexane ring which the alternative 1,5-hydrogen abstraction would not require. The reason for this unusual preference appears to be two-fold: firstly, the 1,6-abstraction, in contrast to the 1,5-abstraction, generates an allylically stabilised radical; secondly, the conformation required for the 1,5-abstraction, in contrast to that for the 1,6-abstraction, would involve prohibitive non-bonded interactions; finally, within the subset of conformations of **10** featuring an axial hexahydrofluorenone residue on the cyclohexane ring, the energetically most favourable one has the hydrogen atom which is to suffer 1,6-abstraction ideally placed in the plane of the carbonyl group and close to the carbonyl oxygen.

The reaction path leading to **10** remains to be discussed. According to its molecular structure, **10** is a dimer formed from two monomeric precursors, the first of which might a priori be either **1** or **2** and the second one either **3**, **4**, or **5**. Of these we can eliminate **5** since it has previously proven inert during irradiation [2]. We can eliminate **3**, furthermore, since both carbon atoms that were to form the new bond, viz. the β-carbon atom in **1** or **2** and the terminal allylium carbon in **3**, would be electrophilic. A dark reaction between **1** and **4** has also been ruled out in our earlier work [2]. The only remaining possibility is reaction between **2** and **4**. In a broad sense, this reaction can be classified as a Michael-type addition, but to the best of our knowledge there is no closely related precedent, except for a minor side-reaction which we encountered when irradiating a substituted derivative of **1** in the presence of phenol (which can play the role of an enol) [7]. On this occasion, we should also mention the addition of enol ethers to **2** which takes an entirely different course [7,8].

The facile oxidation of the kinetically stable enols **4**, **10**, and **13** by atmospheric (i.e. triplet ground-state) oxygen (see also our previous paper [2]) has precedent among aryl-substituted enols [9,10]. It is remarkable since it contrasts with the behaviour both of simple enol ethers and of thermodynamically stable enols (such as simple phenols, 2-hydroxy-cycloalk-2-en-1-ones, and enol forms of 1,3-diones), all of which are stable towards atmospheric oxygen. The oxidation can be proposed to proceed as outlined in Scheme 3. The first step, viz. one-electron oxidation of the π system and proton transfer from the σ system which is orthogonal to the π system, affords the explanation for the observed contrast: proton transfer is impossible with enol ethers, and electron transfer requires more energy in the case of the thermodynamically stable enols. Thus, 1-phenyl-ethenol, a model compound for **4**, **10**, and **13**, has an ionisation energy of 8.01 eV [11] whereas phenol has one of 8.70 eV [12].

4. Conclusion

The Michael-type addition reaction between the highly strained 1-benzoyl-*trans*-cyclohexene **2** and enol **4** is a side-reaction given by the primary photoproduct and a secondary intermediate of the photo-Nazarov cyclisation of **1** in acetonitrile. It leads to the products shown in Scheme 2 essentially via one single primary adduct, **10**. The kinetically stable enols, **4**, **10**, and **13**, in contrast to thermodynamically stable enols and to enol ethers, are sensitive to atmospheric oxygen; an explanation is given.

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