ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 123 (1999) 31–37

Journal of Photochemistry and Photobiology A:Chemistry

Photochemistry of 1-cyclohexenyl phenyl ketone in enol ether solvents. Trapping of the primary photoproduct by formation of [4+2] adducts in high yields

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

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

Received 9 November 1998; received in revised form 13 November 1998; accepted 9 February 1999

Abstract

Photolysis (>300 nm) of 1-cyclohexenyl phenyl ketone (**1**) in ethyl vinyl ether (EVE) or in the methyl homologues of EVE, ethyl *E*-1-propenyl ether and ethyl *Z*-1-propenyl ether, in each case gives exactly two stereoisomers of the [4 + 2] head-to-head adducts of the enol ether double bond to the olefin-carbonyl moiety of **1**. The two stereoisomers obtained from the *E*-propenyl ether are different from the two stereoisomers obtained from the *Z*-propenyl ether; all four of them arise from suprafacial addition to the enol ether double bond. As shown in some detail in the case of EVE, besides the two [4 + 2] adducts smaller amounts of other products are formed, some of which have been known before from the enol ether-free system, which stem from the oxyallyl **3** formally derived from **1** by cyclisation. Absolute and relative quantum yields of formation of the diverse products in dependence on EVE concentration allow the conclusion that the photo-intermediate **A** that gives the [4 + 2] adducts with EVE, does so in competition with both reversion of **A** to ground state **1** and with ring closure of **A** to **3**. It is concluded that **A** is the highly strained ground-state *trans* double-bond isomer of **1**, viz. **2**, formed from **1** with a quantum yield of ca. 0.36 in toluene–EVE mixtures. Even in neat EVE, reversion to **1** accounts for about half of the **2**. The cyclisation of **2** to **3** is about three times faster in the polar acetonitrile than in the nonpolar toluene, relative to reversion to **1**.

Keywords: *trans*-1-Cyclohexenyl phenyl ketone; [4 + 2] Cycloaddition; Enol ethers; *cis–trans*-Photoisomerisation; Quantum yield; 2-Oxyallyl

1. Introduction

The near-UV photolysis of 1-cyclohexenyl phenyl ketone (**1**) to give the hexahydrofluorenone **5** has been known for ca. 25 years now [1]. Some years ago, we established the mechanism of this reaction as shown in Scheme 1 [2]. Not included in Scheme 1 are numerous by-products whose molecular structures and modes of formation we have elucidated before [3]. None of these by-products ever accumulates to more than a few percent of the overall product, but together they can quite significantly depress the yield of **5**. We have shown how to suppress the formation of these by-products so as to obtain **5** efficiently and virtually quantitatively [2]. The latter circumstance could well endow the reaction with synthetic potential when applied to substituted derivatives of **1** [4]. However, there is more than that to the reaction. In our previous work [2], we trapped the intermediates **2** and **3** by adduct formation with added cyclopentadiene; this was done in order to elucidate the mechanism of the photoreaction of **1**. It occurred to us that by trapping **2**, **3**, or **4** with various other agents we might create a whole family of new and possibly useful reactions and at the same time learn more about the transient intermediates. Simple enol ethers appeared to be promising candidates as trapping agents. In the present article, we report on the photolysis of **1** in the presence of these compounds.

2. Experimental

2.1. Preparative experiments

2.1.1. General aspects

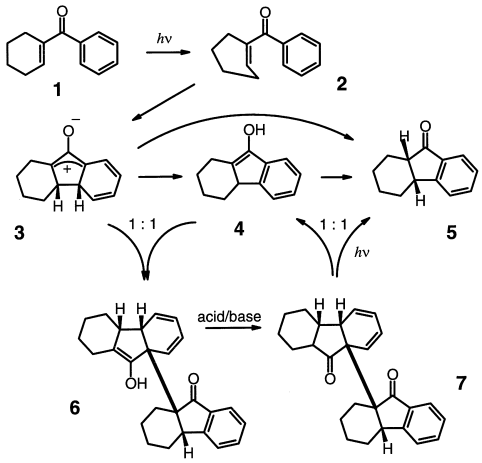
Reactants:

1-Cyclohexenyl phenyl ketone was prepared as described [2]. Ethyl vinyl ether (EVE, Fluka) was redistilled before use.

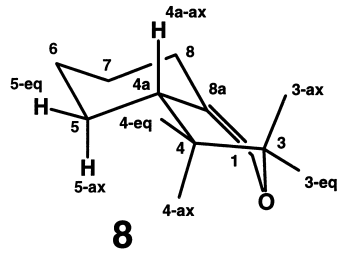
*Corresponding author.

[1]Co-corresponding author. On leave from Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt, in 1994 and 1996.

1010-6030/99/$ – see front matter
PII: S1010-6030(99)00037-4



Scheme 1.



	3-ax	3-eq	4-ax	4-eq
a	OEt	H	H	H
b	H	OEt	H	H
c	H	OEt	Me	H
d	OEt	H	H	Me
e	OEt	H	Me	H
f	H	OEt	H	Me

Fig. 1. Molecular conformation and numbering of positions for adducts **8a–f**. Rear substituents including the 1-phenyl group are omitted for clarity.

Ethyl 1-propenyl ether (3 : 1 *Z*/*E*-mixture, Aldrich) was separated into the two isomers to better than 99.5% isomeric purity by preparative g.l.c. (*Z* elutes before *E*). ^{1}H-NMR: δ values ($CDCl_3$) for α-O olefinic H, β-O olefinic H, O–CH_2, propenyl–CH_3, ethoxy–CH_3, respectively: *Z*: 5.91, 4.34, 3.74, 1.55, and 1.22; *E*: 6.16, 4.72, 3.64, 1.50, and 1.21. The assignment of the two isomers to the *Z* and *E* configurations has been based on the characteristic out-of-plane H–C=C–H vibrations in their infrared spectra [5,6]. The H–C=C–H $J_{H,H}$ values that we observe, 12.5 Hz for *E* and 6.5 Hz for *Z*, support this assignment. However, the δ values for the α-O olefinic protons, 5.91 in '*Z*' and 6.16 in '*E*' suggested the reverse assignment, taking into account ample experience with olefin *Z*/*E* isomer pairs. ^{1}H-NOE experiments then proved the correctness of the original assignment: the two olefinic protons showed a mutual enhancement in the *Z* isomer but not in the *E* isomer; the β-O olefinic proton and the O–CH_2 protons showed a mutual enhancement in the *E* isomer but not in the *Z* isomer.

Irradiations

Solvents: Merck 'Uvasol', used as received.

Apparatus: Immersion well reactor (50 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. This apparatus provides a continuous range of light at >300 nm in the irradiated solution.

Monitoring: Thin-layer chromatography using silica gel ready-made plates (Merck), dichloromethane.

Preparative chromatography

Automatic fraction collector 'Super Frac' (Pharmacia Biotech); silica gel 0.04–0.063 mm (Kieselgel 60 'Merck') used as received; *n*-pentane + (0–6)% ether. *n*-Pentane and diethyl ether were redistilled before use.

NMR of products

Bruker AM 400, operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C. Besides ^{1}H and ^{13}C-BB (broad-band decoupled) spectra, also ^{13}C-DEPT (distortionless enhanced polarisation transfer), C,H-correlation, and H,H-COSY (COrrelation SpectroscopY) experiments were carried out for every pure new compound in order to facilitate assignments of resonances to individual atoms. H,H–spin-spin decoupling experiments for individual H resonances were carried out whenever helpful.

Presentation of NMR data

Compounds **8a–f**, **9**, and **11b**: δ values given below are one for one atom unless specified otherwise and are followed by the positional assignment in brackets (for the numbering of positions, see the Fig. 1). $J_{H,H}$ values are given in Hz and are followed by the two partner position numbers in brackets. Compounds **10** and **11a**: conventional presentation.

*2.1.2. (3α,4aα)- and (3α,4aβ)-3-Ethoxy-4,4a,5,6,7,8-hexahydro-1-phenyl-3H-isochromene (***8a** *and* **8b***), and 9a-(1-ethoxyethyl)-1,2,3,4,4a,9a-hexahydro-9H-fluoren-9-one (***9***)*

1000 mg (5.37 mmol) **1** dissolved in 40 ml EVE was irradiated for 6 h after which time 99% of **1** had reacted and 72% of **1** was transformed into a 3.3 : 1 mixture of **8a** and **8b** (NMR of the crude product). Evaporation at <30°C (rotatory evaporator) and chromatography using 140 g silica gel and *n*-pentane + 2% diethyl ether as the eluent afforded, after 11 mg unidentified material, 790 mg (57%) of a 3.3 : 1 mixture of **8a** and **8b**. Further elution afforded 10 mg unidentified, 7 mg **1**, 10 mg unidentified, 23 mg (1.7%) **11a** (75% with 25% of a stereoisomer) 25 mg **7**, (continued with 4% diethyl ether) 70 mg (5%) **9**, followed by altogether 190.5 mg unidentified material. Chromatography of the mixture of **8a** and **8b** using *n*-pentane + 1% diethyl ether as the eluent afforded partial separation into 39% **8a** (100% pure by NMR, eluted first), 45% mixture, and 16% **8b** (97% pure by NMR; 3% **8a** as the contaminant). Both **8a** and **8b** are liquids.

NMR data in $CDCl_3$:

8a: ^{1}H: δ: 7.33 (4 H, *o*- and *m*-phenyl), 7.27 (*p*-phenyl), 5.07 (3-eq), 3.96 and 3.65 (O–CH_2), 2.51 (8-eq), 2.27 (4a-ax), 2.01 (4-eq), 1.89 (5-eq), 1.81 (8-ax), 1.78 (6-eq), 1.72 (7-eq), 1.62 (4-ax), 1.38 (6-ax), 1.25 (3 H, CH_3), 1.24 (7-ax), 1.12 (5-ax). Selected $J_{H,H}$ values: 2.5 (3-eq; 4-ax), 3.9 (3-eq; 4-eq), 13.5 (4-ax; 4-eq), 9.3 (4-ax; 4a-ax), 6.7 (4-eq; 4a-ax), 12.5 (4a-ax; 5-ax), 4.5 (4a-ax; 5-eq) 1.4 (4a-ax, 8-ax), 14 (8-ax, 8-eq) 13.3 (8-ax, 7-ax), 4.5 (8-ax, 7-eq), 3.7 (8-eq, 7-ax),

2.5 (8-eq, 7-eq) 2.1 (8-eq, 6-eq); all other $J_{H,H}$ values are in the ranges expected for the conformation given in the Fig. 1.

^{13}C: δ: 141.9 (1), 136.6 (ipso-phenyl), 129.1 and 127.8 (4 C, *o*- and *m*-phenyl), 127.6 (*p*-phenyl), 113.9 (8a), 96.5 (3), 63.6 (O–CH_2), 35.4 (4), 34.9 (5), 30.5 (4a), 28.9 (8), 27.4 (7), 26.2 (6), 15.2 (methyl).

8b: ^{1}H: δ: 7.35 (2 H, *o*-phenyl), 7.31 (2 H, *m*-phenyl), 7.27 (*p*-phenyl), 4.96 (3-ax), 4.01 and 3.63 (O–CH_2), 2.57 (8-eq), 2.24 (4a-ax), 2.13 (4-eq), 1.91 (5-eq), 1.79 (6-eq), 1.74 (2 H, 7-eq and 8-ax), 1.60 (4-ax), 1.35 (6-ax), 1.29 (7-ax), 1.25 (5-ax), 1.25 (3 H, CH_3). Selected $J_{H,H}$ values: 8.4 (3-ax, 4-ax), 2.0 (3-ax, 4-eq), 13 (4-ax, 4-eq), 9.2 (4-ax, 4a-ax), 7.4 (4-eq, 4a-ax), 12 (4a-ax, 5-ax), 3.5 (4a-ax, 5-eq), 1.0 (4a-ax, 8-ax).

^{13}C: δ: 142.8 (1), 136.2 (ipso-phenyl), 128.9 (2 C, *o*-phenyl), 127.8 (2 C, *m*-phenyl), 127.6 (*p*-phenyl), 113.6 (8a), 99.2 (3), 64.1 (O–CH_2), 36.7 (4), 35.1 (4a), 34.9 (5), 29.1 (8), 27.5 (7), 26.3 (6), 15.2 (methyl).

9: ^{1}H: δ: 7.69 (8), 7.56 (6), 7.45 (5), 7.32 (7), 3.64 (9aα), 3.61 (4a), 3.47 and 3.22 (O–CH_2), 1.07-1.92 (8 H, 1-4), 1.22 (3 H, 9aβ-CH_3), 0.92 (3 H, ethoxy–CH_3).

^{13}C: δ: 210.8 (9), 158 (4b), 136.8 (8a), 134.4 (6), 127 (7), 124.9 (5), 123.5 (8), 78.9 (9aα), 64.7 (O–CH_2), 57.3 (9a), 39.4 (4a), 26.4, 26.1, 19.4, 18.6 (1-4), 15.4 (ethoxy–methyl), 15.3 (9aβ).

11a (main stereoisomer in the mixture): ^{1}H: δ: 7.89 (d; 8 Hz; 2 H), 7.45 (mc; 3 H), 6.14 (*d*; 12.6 Hz; 1 H), 4.49 (*dd*; 12.6 Hz, 8.7 Hz; 1 H), 3.0–3.5 (*m*; 4 H), 1.1–1.9 (*m*; 8 H), 1.06 (*t*; 7 Hz; 3 H).

*2.1.3. (3α,4α,4aβ)- and (3α,4α,4aα)-3-Ethoxy-4,4a,5,6,7,8-hexahydro-4-methyl-1-phenyl-3H-isochromene (***8c** *and* **8d***)*

1000 mg (5.37 mmol) **1** dissolved in 40 ml ethyl *Z*-1-propenyl ether was irradiated for 6.5 h after which time all **1** had reacted and 49% of it was transformed into a 1 : 1.6 mixture of **8c** and **8d** (NMR of the crude product). Evaporation at <30° and chromatography using 170 g silica gel and *n*-pentane + 2% diethyl ether as the eluent afforded 618.4 mg of a 90% pure (corresponding to 38%) 1 : 1.6 mixture of **8c** and **8d**, whereupon the chromatography was discontinued. Chromatography of the mixture of **8c** and **8d** using *n*-pentane + 1% diethyl ether as the eluent resulted in purification and partial separation and afforded enriched samples of **8c** (eluted first) and **8d** (each sample was 95% pure by NMR with 5% of the other diastereomer as the contaminant). Both samples were liquids.

NMR data in $CDCl_3$

8c: ^{1}H: δ: 7.32 (4H, *o*- and *m*-phenyl), 7.25 (*p*-phenyl), 4.87 (3-ax), 3.98 and 3.58 (O–CH_2), 2.55 (8-eq), 2.18 (4a-ax), 2.15 (4-eq), 1.80 (2 H, 5-eq and 6-eq), 1.79 (8-ax), 1.70 (7-eq), 1.49 (5-ax), 1.29 (6-ax), 1.24 (7-ax), 1.24 (3 H, ethoxy CH_3), 0.98 (3 H, 4-ax-CH_3). Selected $J_{H,H}$ values: 2.3 (3-ax, 4-eq), 6.8 (4-eq, 4-ax-CH_3), 6.9 (4-eq, 4a-ax), 12.4 (4a-ax, 5-ax), 3.0 (4a-ax, 5-eq), 1.0 (4a-ax, 8-ax), 13.7 (8-ax, 8-eq), 12.3 (8-ax, 7-ax), 4.5 (8-ax, 7-eq), 3.3 (8-eq, 7-ax), 3.3 (8-eq, 7-eq), 1.7 (8-eq, 6-eq).

^{13}C: δ: 141.6 (1), 136.5 (ipso-phenyl), 129.1 and 127.8 (4 C, *o*- and *m*-phenyl), 127.5 (*p*-phenyl), 113.2 (8a), 101.6 (3), 64.0 (O–CH_2), 39.0 (4a), 35.3 (4), 29.9 (8), 28.9 (5), 27.9 (7), 26.8 (6), 15.3 (2 C, 2 methyl).

8d ^{1}H: δ: 7.33 (4 H, *o*- and *m*-phenyl), 7.27 (*p*-phenyl), 4.84 (3-eq), 3.95 and 3.64 (O–CH_2), 2.51 (8-eq), 2.03 (5-eq), 1.84 (4a-ax), 1.82 (6-eq), 1.75 (8-ax), 1.72 (7-eq), 1.66 (4-ax), 1.32 (6-ax), 1.28 (7-ax), 1.23 (3 H, ethoxy–CH_3), 1.01 (5-ax), 1.01 (3 H, 4-eq-CH_3). Selected $J_{H,H}$ values; 2.5 (3-eq, 4-ax), 6.5 (4-ax, 4-eq-CH_3), 9.3 (4-ax, 4a-ax), 12.5 (4a-ax, 5-ax), 4.5 (4a-ax, 5-eq), 1.0 (4a-ax, 8-ax), 14.3 (8-ax, 8-eq), 3.7 (8-eq, 7-ax), 2.5 (8-eq, 7-eq), 1.8 (8-eq, 6-eq).

^{13}C: δ: 141.2 (1), 136.7 (ipso-phenyl), 129.1 and 127.8 (4 C, *o*- and *m*-phenyl), 127.5 (*p*-phenyl), 113.7 (8a), 99.6 (3), 63.9 (O–CH_2), 38.7 (4), 37.7 (4a), 33.2 (5), 29.0 (8), 27.7 (7), 26.2 (6), 15.2 (ethoxy–methyl), 14.4 (4-eq-methyl).

*2.1.4. (3α,4β,4aα)- and (3α,4β,4aβ)-3-Ethoxy-4,4a,5,6,7,8-hexahydro-4-methyl-1-phenyl-3H-isochromene (***8e** *and* **8f***) and cis-2-(2-ethoxy-1-methyl-ethenyl)-cyclohexyl phenyl methanone (***11b***)*

1000 mg (5.37 mmol) **1** dissolved in 40 ml ethyl *E*-1-propenyl ether was irradiated for 3.5 h after which time all **1** had reacted and 59% of it was transformed into a 1 : 1.8 mixture of **8e** and **8f** (NMR of the crude product). Evaporation at <30° and chromatography using 170 g silica gel and *n*-pentane + 2% diethyl ether as the eluent afforded 604.3 mg (41%) of a 1 : 1.8 mixture of **8e** and **8f** followed by 34 mg (2.3%) of **11b**, whereupon the chromatography was discontinued. Chromatography of the mixture of **8e** and **8f** using *n*-pentane + 1% diethyl ether as the eluent resulted in partial separation and afforded enriched samples of **8e** (eluted first) and **8f** (each sample was 95% pure by NMR with 5% of the other diastereomer as the contaminant). Both samples were liquids.

NMR data in $CDCl_3$

8e: ^{1}H: δ: 7.31 (4 H, *o*-and *m*-phenyl), 7.25 (*p*-phenyl), 4.78 (3-eq), 3.95 and 3.64 (O–CH_2), 2.52 (8-eq), 2.35 (4a-ax) 1.97 (4-eq), 1.83 (2 H, 6-eq and 8-ax), 1.72 (5-eq), 1.67 (7-eq), 1.35 (6-ax), 1.25 (5-ax), 1.24 (3 H, ethoxy CH_3), 1.17 (7-ax), 0.96 (3 H, 4-ax-CH_3). Selected $J_{H,H}$ values: 4.1 (3-eq, 4-eq), 7.12 (4-eq, 4-ax-CH_3), 6.45 (4-eq, 4a-ax), 12.4 (4a-ax, 5-ax), 4.4 (4a-ax, 5-eq), 1.5 (4a-ax, 8-ax), 14 (8-ax, 8-eq), 13 (8-ax, 7-ax), 4.3 (8-ax, 7-eq), 3 (8-eq, 7-ax), 3 (8-eq, 7-eq), 2.4 (8-eq, 6-eq).

^{13}C: δ: 141.2 (1), 136.6 (ipso-phenyl), 129.1 and 127.8 (4 C, *o*-and *m*-phenyl), 127.5 (*p*-phenyl), 112.3 (8a), 101.3 (3), 63.7 (O–CH_2), 35.2 (4), 35.0 (4a), 29.0 (8), 28.7 (5), 27.2 (7), 26.3 (6), 15.3 (ethoxy–methyl), 12.5 (4-ax-methyl).

8f: ^{1}H: δ: 7.34 (4 H, *o*- and *m*-phenyl), 7.26 (*p*-phenyl), 4.56 (3-ax), 4.02 and 3.63 (O–CH_2), 2.58 (8-eq), 2.04 (5-eq), 1.83 (6-eq), 1.73 (7-eq), 1.71 (4a-ax), 1.70 (8-ax) 1.58 (4-ax), 1.32 (2 H, 6-ax and 7-ax), 1.26 (3 H, ethoxy–CH_3), 1.16 (5-ax), 1.04 (3 H, 4-eq-CH_3). Selected $J_{H,H}$ values: 7.76 (3-ax, 4-ax), 6.64 (4-ax, 4-eq-CH_3), 8.4 (4-ax, 4a-ax), 12 (4a-ax, 5-ax) 3.5 (4a-ax, 5-eq).

^{13}C: δ: 142.5 (1), 136.1 (ipso-phenyl), 128.9 and 127.8 (4 C, *o*- and *m*-phenyl), 127.6 (*p*-phenyl), 113.6 (8a), 103.4 (3), 64.4 (O–CH_2), 43.2 (4a), 40.1 (4), 33.5 (5), 29.2 (8), 27.8 (7), 26.5 (6), 15.5 (ethoxy–methyl), 15.1 (4-eq-methyl).

11b: ^{1}H: δ: 7.87 (2 H, *o*-phenyl), 7.47 (*p*-phenyl), 7.38 (2 H, *m*-phenyl), 5.63 (olefinic), 4.01 (1) 3.64 and 3.58 (2 H, O–CH_2), 2.97 (2), 2.19 and 1.49 (3), 1.83 and 1.35 (4), 1.73 and 1.44 (5), 1.83 and 1.73 (6), 1.40 (3 H, olefinic CH_3), 1.14 (3 H, ethoxy–CH_3). Selected $J_{H,H}$ values: 4.9 (1, 2), 2 × 4.2 (1, 6), 11.7 and 4.2 (2, 3).

^{13}C: δ: 204.6 (C=O), 140.8 (α-O-olefinic), 138.5 (ipso-phenyl), 132.7 (*p*-phenyl), 128.2 and 128.1 (4 C, *o*- and *m*-phenyl), 116.7 (β-O-olefinic), 67.2 (O–CH_2), 43.3 (1), 38.1 (2), 28.6 (6), 26.0 and 25.9 (3 and 4), 21.7 (5), 16.0 (olefinic methyl), 15.3 (ethoxy-methyl).

2.1.5. *Photoreaction of* **1** *with 0.68 M EVE in acetonitrile*

A solution of 1000 mg (5.37 mmol) **1** and 2250 mg (31.2 mmol) EVE in 42.8 ml acetonitrile was irradiated for 2 h after which time 65% of the **1** had reacted. **5** and **6** were the main products, **7** was a minor product, and **8a** + **8b** was an even lesser product (NMR of the crude reaction product). Removal of the solvent and chromatography using 70 g silica gel and *n*-pentane + 2% diethyl ether as the eluent gave: 5.2 mg unidentified, followed by 26.4 mg **8a** + **8b** (3.3 : 1), 247 mg **1**, 510 mg **5** + **7** (ca. 1 : 1; all **6** had been converted to **7** on contact with the silica gel), 48 mg **9**, (continued with *n*-pentane + 5% diethyl ether) 4.8 mg unidentified, 23.8 mg new photodimer of **1** to be described elsewhere [3], 12 mg unidentified, 11.6 mg **10** + unidentified (ca. 1 : 1), 23 mg unidentified, 85 mg new photodimer of **1** to be described elsewhere [3], 28 mg hydroxy-**7** (arising from air oxidation of **6** [2]), 14 mg unidentified. **10**: ^{1}H: δ in $CDCl_3$: 7.71 (*d*, 8 Hz, 1 H), 7.56 (*t*, 2 × 8 Hz, 1 H), 7.44 (*d*, 8 Hz, 1 H), 7.33 (*t*, 2 × 8 Hz, 1 H), 3.41 and 3.38 (A_2B_2 system, $J_{A,B'} \cong J_{A,B} \cong 8$ Hz), 3.30 (*m*, 1 H), 3.29 (*q*, 3 × 7.7 Hz, 2 H), 0.8-2.0 (*m*, 8 H), 1.03 (*t*, 2 × 7.7 Hz, 3 H).

2.2. *Elucidation of molecular structures*

The NMR data given above, combined with the ^{13}C-DEPT and C,H-correlation NMR spectra for each compound, sufficed to establish the molecular constitution (excluding stereochemistry) of adducts **8a–f** unambiguously. In the case of **8a**, a virtually complete unravelling of the H,H spin-coupling pattern was possible; this pattern allowed assignments of all resonances to individual positions in the molecule; moreover, it established the chair conformation for the cyclohexane ring (see Fig. 1). The 4a-H occupies an axial position in this chair, as revealed by its coupling of 12.5 Hz, characteristic for a *trans*-diaxial arrangement, to the 5-H at $\delta = 1.12$. Of the two couplings of the 4a-H to the two 4-H , the larger one (9.3 Hz) again is characteristic for a *trans*-diaxial arrangement which establishes the half-chair conformation of the dihydropyrane ring as shown in the Fig. 1. The hydrogen thus identified as the 4-ax-H shows a small coupling of 2.5 Hz to 3-H in the major EVE adduct and a large one of 8.4 Hz, again characteristic for a *trans*-diaxial arrangement, to 3-H in the minor EVE adduct. This establishes the molecular structures **8a** for the former and **8b** for the latter. A complete unravelling of the entire H,H spin-coupling pattern as in **8a** was not possible in **8b–f** because of strong overlap of some mutually strongly coupled signals, but the important region of positions 3, 4, 4a, 5 was always clear. The strong similarity of all observed NMR parameters (except for the discriminating region of positions 3, 4, 4a, 5) in all six compounds **8a–f** however establishes that, as might have been expected, they all have the same chair/half-chair conformation shown in the Fig. 1. (In particular, note the couplings for 4a-H of 12-12.5 Hz to 5-ax-H, of 3-4.5 Hz to 5-eq-H, and of 1-1.5 Hz to 8-ax-H in all six compounds.) The four isomers, **8c–f**, represent the complete set of possible diastereomers for their common molecular constitution. Of these four, the two showing the larger couplings between 4-H and 4a-H, 9.3 and 8.4 Hz, must be **8d** and **8f** (where 4-H = 4-ax-H) whereas the two showing the smaller couplings, 6.9 and 6.45 Hz, must be **8c** and **8e** (where 4-H = 4-eq-H). Of the pair **8d** and **8f**, one isomer shows a small coupling of 2.5 Hz between 4-ax-H and 3-H whereas the other shows a large one of 7.76 Hz, consistent with a *trans*-diaxial arrangement. The former therefore must be **8d** and the latter **8f**. In the pair, **8c** and **8e**, both isomers show small couplings between 4-eq-H and 3-H of 2.3 and 4.1 Hz, respectively, as might have been expected. The assignment of the individual members of this pair to the molecular structures **8c** or **8e** is consistently achieved in any of three independent ways: Comparison of the two 4-eq-H/3-H couplings in **8c** and **8e** with the corresponding values in **8a** and **8b**; comparison of the two δ values for 4-eq-H in **8c** and **8e** with the corresponding values in **8a** and **8b**; comparison of the two δ values for 4a-H in **8c** and **8e** with the corresponding values in **8d** and **8f**. Comparisons among the ^{13}C δ values for C-3, C-4, C-4a, and C-5 of all six adducts **8** verify the above analysis.

The molecular constitutions of **9** and **11b** follow from the ^{1}H-, *13*C-BB, ^{13}C-DEPT, and C,H-correlation NMR spectra, in case of **9** aided by comparison with those of analogous compounds [2]. The molecular constitutions of **10** and **11a**, which were obtained only in mixtures, follow from their plain ^{1}H NMR spectra, aided in the case of **10** by comparison with those of analogous compounds [2].

2.3. *Analytical experiments*

2.3.1. *Absolute quantum yields of the decrease of* **1**

Automatic electronically integrating actinometer [7], calibrated at 365 nm using the ferrioxalate method. [**1**] = 5 mM, 1 cm cuvette, irradiation wavelength 365 nm. Analysis by monitoring the decrease of the UV absorption of the cuvette containing the solution at 334 nm, close to the first absorption maximum of **1**, until constancy

of that absorption. From the initial absorption, A_0, the absorption after a certain number of quantum counts, A_C, and the final constant absorption, A_∞, one obtains the relative amount of **1** that has disappeared, as $(A_0\text{-}A_C)/(A_0\text{-}A_\infty)$. For the calculation of the quantum yield of disappearance of **1**, the initial linear part of the decrease as a function of the number of quantum counts was used.

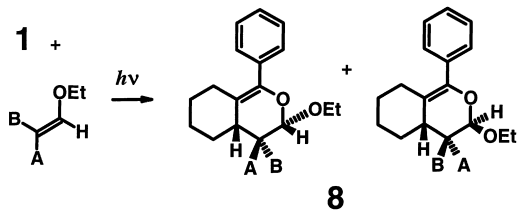
2.3.2. Dependence of product ratios and relative quantum yields on EVE concentration

Merry-go-round apparatus with a central 125 W mercury high-pressure lamp (Philips HPK 125), solidex glassware, irradiation wavelength: continuum, >300 nm. Series of solutions of constant [**1**] (0.1 M) and variable [EVE] (>0.5 M) in toluene or acetonitrile, constant irradiation time (6 h) after which roughly half of the **1** in every solution had reacted. Quantitative analysis by 400 MHz ^{1}H spectroscopy in $CDCl_3$ after evaporation of solvent and EVE, making use of the highly characteristic signals in the region of $\delta = 2.5$–6.8 and checking the result against the integrals above and below that region.

3. Results

The irradiation of **1** in the neat enol ethers gives good yields (49-72% according to analysis, 38-57% isolated) of adducts **8** (Scheme 2) which are stable under the conditions of formation and workup. Compounds **8** result from a [4 + 2] cycloaddition of **1** or **2** to the enol ether. Exactly two stereoisomers of **8** are formed in each case, all of which result from suprafacial addition (i.e., both new single bonds are formed from the same face of the adding π bond) to the enol ether double bond. Since a contamination of **8c** + **d** by more than 0.5% **8e** or **8f** would have been detected, and vice versa, the suprafacial addition is highly stereoselective.

Besides, compounds **5**, **6**, and **7** are formed as minor products; these have been known before [2] to arise on irradiation of **1** in the absence of enol ethers via the oxyallyl **3** and the enol **4** (Scheme 1). The ratio of **5** to **6** + **7** (T in Table 1) is found at ca. 1 : 2, independent of solvent (aceto-

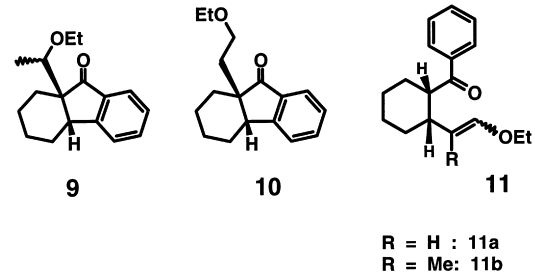


8

A:	B:	% yield*)				
H	H	72 (57)	(**8b**)	1	: 3.3	(**8a**)
H	Me	49 (38)	(**8c**)	1	: 1.6	(**8d**)
Me	H	59 (41)	(**8f**)	1.8	: 1	(**8e**)

*)mixture of both isomers; isolated yield in parentheses

Scheme 2.



9 **10** **11**

R = H : 11a
R = Me: 11b

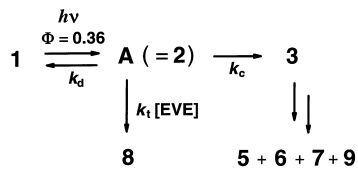
Scheme 3.

nitrile, EVE, toluene). In addition, compounds **9**, **10** and **11a** (in the case of EVE; Scheme 3) are formed as minor products of which **10** and **11a** are formed only in negligible amounts and were not obtained pure. The ratio of **9** to **5** + **6** + **7** (S in Table 1) is found to be approximately proportional to [EVE] and independent of solvent (acetonitrile, EVE, toluene). **9** appears to arise from a thermal reaction of EVE with enol **4** in analogy to the known thermal addition of an other simple enol ether to the stable enol dimedone [8]. A photochemical reaction of EVE with **4** or a thermal reaction of EVE with **3** can be expected to lead to **10** [9].

In the case of toluene as the solvent, the ratio of **8a** + **b** to all products that arise via oxyallyl **3**, viz. **5** + **6** + **7** + **9** (neglecting **10** and **11a**; R in Table 1), is found to be proportional to [EVE]. This is consistent with a mechanism by which both **8a** + **b** and **3** are formed from a common precursor, **A** (see below), in a ratio $\underline{R} = k_t[EVE]/k_c$ ('t' for trapping by EVE, 'c' for cyclisation to **3**):

$$\frac{[\mathbf{8}a + b]}{([\mathbf{5} + \mathbf{6} + \mathbf{7} + \mathbf{9}][EVE])} = \frac{\underline{R}}{[EVE]} = \frac{k_t}{k_c} \quad (1)$$

k_t/k_c (see Table 1) is thus found to be independent of [EVE] in toluene, but to be lower by a factor of ca. 10 in the polar acetonitrile, where it continuously rises upon increase of the content of the less polar EVE until, in neat EVE, it is lower by a factor of two than in the still less polar toluene/EVE mixtures. Another point to be noted from Table 1 is that the amount of **1** that had reacted increases with the concentration of [EVE]. This indicates that **A** not only cyclises to **3** and is trapped by EVE to give **8a** + **b**, but that it also reverts to **1**. The simplest reaction scheme to account for all these observations is the one given in Scheme 4, where the identity of **A** still needs to be clarified and the quantum yield still needs to be determined.



Scheme 4.

Table 1
Analytical experiments (merry-go-round apparatus, 0.1 M **1**, 6 h irradiation with >300 nm). The amounts of **10** and **11a** were too low to be detected and were neglected. In the case of **6** + **7**, percentages and ratios refer to C_{13} units

No.	So.[a]	[EVE]/ M	Percentage in product mixture					$\underline{R}$[d]	$\underline{S}$[e]	$\underline{T}$[f]	$[\mathbf{1}]_0/([\mathbf{1}]_0-[\mathbf{1}])$	k_t/k_c	k_d/k_c	k_d/k_t
			1	**5**	**6** + **7**	**8a** + **b**	**9**							
1	AN[b]	0.53	58.4	12.5	24.8	1.0	3.5	0.0248	0.094	0.50	2.404	0.0468	1.809	38.66
2	AN[b]	1.06	54.5	12.7	23.9	2.2	6.7	0.0516	0.184	0.53	2.198	0.0487	1.607	33.01
3	AN[b]	2.65	54.8	10.4	18.2	6.1	10.4	0.156	0.364	0.57	2.212	0.0589	1.786	30.34
4	AN[b]	5.30	51.4	6.7	11.8	14.2	15.8	0.414	0.851	0.57	2.058	0.0781	1.933	24.74
5	neat EVE	10.6	47.3	1.8	3.6	38.4	8.9	2.690	1.670	0.50	1.897	0.254	4.365	17.20
6	Tol[c]	5.30	52.1	2.1	4.2	34.9	6.8	2.680	1.083	0.50	2.088	0.506	5.158	10.20
7	Tol[c]	2.65	63.6	3.2	6.8	21.2	5.3	1.389	0.532	0.47	2.747	0.524	5.161	9.85
8	Tol[c]	1.06	72.3	4.5	9.6	10.5	3.0	0.614	0.213	0.47	3.610	0.579	5.089	8.79
9	Tol[c]	0.53	77.4	5.2	11.3	12.7	1.4	0.263	0.086	0.46	4.425	0.496	5.166	10.41

[a] Solvent.
[b] Acetonitrile.
[c] Toluene.
[d] [**8a** + **b**]/[**5** + **6** + **7** + **9**].
[e] [**9**]/[**5** + **6** + **7**].
[f] [**5**]/[**6** + **7**].

Under the assumption that the rate of photoconversion of **1** to **A** ('*hν*' in Scheme 4) is independent of the solvent (acetonitrile, EVE, toluene), Scheme 4 leads to the following expression:

$$\frac{[\mathbf{1}]_0}{([\mathbf{1}]_0 - [\mathbf{1}])} = b + b\left(\frac{k_d}{k_c}\right)(1 + \underline{R})^{-1} \quad (2)$$

where b is a proportionality constant. In the solvent system toluene–EVE, the dependence of $[\mathbf{1}]_0/([\mathbf{1}]_0-[\mathbf{1}])$ on $(1 + \underline{R})^{-1}$ according to Eq. (2) shows very good linearity ($r^2 = 0.99963$), which means that in this solvent system the above two assumptions (validity of Scheme 4 and constant rate of photoconversion of **1** to A) are correct and that in addition k_d/k_c does not vary with the EVE content. Linear regression yields $b = 0.869 \pm 0.034$ and $k_d/k_c = 5.141 \pm 0.215$. The quantity b, which contains the rate of photoconversion of **1** to **A**, depends on our experimental settings and is not further analysed here. After rearrangement of Eq. (2) so as to make it explicit in k_d/k_c and assuming the same value for b to hold not only for the toluene–EVE systems but for all solvent systems in Table 1, one can calculate a value for k_d/k_c for every single run in Table 1, and these values are given there. Also given are values for k_d/k_t, obtained from k_d/k_c and k_t/k_c.

The absolute quantum yield of 0.163 was found for the disappearance of **1** in neat EVE. From this value and the values for the percentage of **1** in the product mixtures as given in Table 1, one can calculate the corresponding quantum yield for every run given in Table 1. One thus finds 0.128 and 0.0698 for 0.53 M EVE in acetonitrile and in toluene, respectively. Using the $\underline{R}$ and k_d/k_c values for these two runs, one can obtain from their two quantum yields the quantum yields for neat (without EVE) acetonitrile and toluene as 0.126 and 0.058, respectively. The direct determination of these two values by our UV method was too imprecise due to the build-up of the strong absorption by **6**; however, it was possible in acetonitrile containing 1.3 mM *p*-toluene sulphonic acid which converted all **6** to **7**. The value obtained for this system, 0.139, is slightly higher than the above value of 0.126 which may be due to some contribution by *p*-toluene sulphonic acid-catalysed cyclisation of **A** to **3**. From the foregoing value for 0.53 M EVE in toluene, 0.0698, and the $\underline{R}$ and k_d/k_c values for this system, 0.263 and 5.166, one obtains the quantum yield of formation of **A** in this system as $0.0698(1 + 5.166/(1 + 0.263)) = 0.355$. The constancy of b within all toluene–EVE systems as found above implies that the value of 0.355 should hold for all these systems. (As for the systems, acetonitrile–EVE and neat EVE, we have assumed the same value for b also to hold for these latter systems, and thus have implicitly assumed the same quantum yield value for them as well. At present, we have no way to determine the values for these systems.)

One can now address the question of the identity of A. The quantum yield for its formation, 0.36, is remarkable in that it is $\ll 1$. This excludes an excited singlet state of **1** as a candidate for **A** since we irradiate into the longest-wavelength UV band of **1**, which means that we create the lowest excited singlet state of **1** at unit quantum yield. It also excludes an excited triplet state because the lowest excited singlet states of α,β-unsaturated ketones and phenyl ketones are known to convert, if they do not react chemically beforehand, to the lowest triplet states within picoseconds and at close to unity quantum yields. This leaves the highly strained ground state double-bond isomer of **1**, viz. **2**, as the only candidate. A stereospecific suprafacial [4 + 2] cycloaddition to EVE and its homologues is exactly what is to be expected of **2**, whereas excited triplet states of **1**

would be expected to give significant amounts of, if not exclusively, [2 + 2] adducts [10–16] and, moreover, would not be stereospecific, and the lowest excited singlet states of conjugated ketones are much too short-lived to give bimolecular reactions. This [4 + 2] cycloaddition of **2** to the enol ethers is also regiospecific in analogy to the closely related thermal hetero Diels–Alder reaction between acrolein and enol ethers [17,18] which is just as regiospecific. Whereas the latter reaction, however, requires temperatures of at least 135°C, the reaction of **2** proceeds at ambient temperature or below due to the high ring strain of **2**. A [4 + 2] cycloaddition between **2** and an enol ether, which is both regio- and stereospecific, still allows two stereoisomers to be formed corresponding to *endo* and *exo* additions. We observe these two stereoisomers in each case, **8a**, **8d**, and **8e** resulting from a *syn* orientation of the enol ether oxygen atom relative to the oxa-diene system of **2** in the reacting complex (*endo*), and **8b**, **8c**, and **8f** resulting from an *anti* orientation (*exo*). Already in our earlier work [2] we had concluded that the photoreactions of **1** (in the absence of enol ethers) proceed via **2** (Scheme 1); the present work corroborates this conclusion. In analogy to the system of 1-cylohexenyl methyl ketone [19] one can conclude that the $^3(\pi,\pi)^*$ state of **1**, the olefinic double bond of which is strongly twisted [20], decays to both **1** and **2** in their electronic ground states. (The $^1(\pi,\pi)^*$ state is energetically above the $^1(n,\pi)^*$ state which we populate directly by irradiation and therefore is not accessible, and neither $(n,\pi)^*$ state will have its olefinic double bond strongly twisted. As is characteristic for conformationally unrestricted states of α,β-unsaturated ketones [20], the reactive excited state in the present case shows no luminescence at 77 K and is not noticeably quenched by 1,3-pentadiene [2]) As the quantum yield of formation of **2** of 0.36 suggests, the ratio of **1** and **2** thus formed from the $^3(\pi,\pi)^*$ state is roughly 2 : 1. The k_d/k_c and k_d/k_t ratios given in Table 1 show that reversion to **1** (k_d) is the predominant reaction of **2** throughout. Even in neat EVE, 54% of the **2** revert to **1**. Another point to be noted from Table 1 is that, relative to k_d, cyclisation of **2** to **3** is roughly three times faster in the polar acetonitrile than in the nonpolar systems. This is understandable since **3** is more polar than **1** and **2** (see Scheme 1). The smallness of the dependence of the rate of the [4 + 2] cycloaddition on solvent polarity, as evident from Table 1, is consistent with its concerted nature. Adducts **11**, by contrast, appear to arise from a two-step addition of enol ether and **2** via a 1,4-dipole as the intermediate.

4. Conclusion

The present work continues on some further aspects of the photochemistry of **1** [2,21,22]. The [4 + 2] cycloaddition reported here carries synthetic potential: The adducts **8** are reactive and conceivably can give a variety of transformations (for some examples with related adducts [23]), the cycloaddition may conceivably be extended to various substituted systems, and the photochemical method allows the preparation of the sensitive adducts of type **8** at drastically lower temperatures than the thermal method (viz. **1** + enol ethers at ca. 200°C). In addition, the present work has led to some quantitative insight into the reactivity of **2** (in particular, the relative rates of cyclisation to **3** and to reversion to **1**) and to the quantum yield of formation of **2**.

Acknowledgements

The authors wish to thank Mr. Jörg Bitter and Mrs. Kerstin Sand for carrying out the NMR experiments, Mr. Dieter Stoffels for the preparative g.l.c. separation of the propenyl ethyl ether stereoisomers, and Mrs. Dagmar Kreft for help with the automatic actinometer. A.A.M. Gaber gratefully acknowledges two grants from DAAD (Deutscher Akademischer Austauschdienst) and DFG (Deutsche Forschungsgemeinschaft).

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: Chem. 57 (1991) 127.
[3] I. Heise, J. Leitich, K. Schaffner, manuscript in preparation.
[4] A.H. Said, PhD. Thesis, Max-Planck-Institut für Strahlenchemie, Ruhr-Universität Bochum, Germany, 1984.
[5] W.L. Howard, E.C. Jacobsen, R.A. Newton, J. Org. Chem. 26 (1961) 3574.
[6] Ruhrchemie AG., German Patent, 1019090 (1955).
[7] W. Amrein, J. Gloor, K. Schaffner, Chimia 28 (1974) 185.
[8] J.T. Pinhey, P.T. Xuan, Aus. J. Chem. 41 (1988) 331.
[9] N.M. Berry, M.C.P. Darey, L.M. Harwood, Tetrahedron Lett. 27 (1986) 2319.
[10] D.R. Julian, R. Foster, J.C.S. Chem. Commun. (1973) 311.
[11] K. Mizuno, H. Okamoto, C. Pac, H. Sakurai, S. Murai, N. Sonoda, Chem. Lett. (1975) 237.
[12] R.J. Atkins, G.I. Fray, A. Gilbert, M.W. bin Samsudin, A.J.K. Steward, G.N. Taylor, J. C.S. Perkin I (1979).
[13] F. Lemaire, R. Stringat, C. Bertaina, R. Fellous, Tetrahedron Lett. 27 (1986) 5847.
[14] D.I. Schuster, G. Lem, N.A. Kaprinidis, Chem. Rev. 93 (1993) 3.
[15] N.A. Kaprinidis, G. Lem, S.H. Courtney, D.I. Schuster, J. Am. Chem. Soc. 115 (1993) 3324.
[16] D. Andrew, A.C. Weedon, J. Am. Chem. Soc. 117 (1995) 5647.
[17] R.I. Longley, W.S. Emerson, J. Am. Chem. Soc. 72 (1950) 3079.
[18] C.W. Smith, D.G. Norton, S.A. Ballard, J. Am. Chem. Soc. 73 (1951) 5267.
[19] R. Bonneau, P. Fornier de Violet, C.R. Acad. Sci. Paris, Ser. C 284 (1977) 631.
[20] R. Bonneau, J. Am. Chem. Soc. 102 (1980) 3816.
[21] J. Leitich, K. Schaffner, Angew. Chem. 105 (1993) 436; J. Leitich, K. Schaffner, Angew. Chem. Int. Ed. Engl. 32 (1993) 441.
[22] J. Leitich, I. Heise, K. Schaffner, Can. J. Chem. 73 (1995) 1785.
[23] M.F. Ansell, B. Gadsby, J. Chem. Soc. (London) (1958) 3388.