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Photoinduced reductions of chalcone derivatives in the presence of amines

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Abstract

Photoinduced electron transfer reactions of chalcone (CH) derivatives (**1a–1e**) with triethylamine (TEA) gave *cis*- and *trans*-2-benzoyl-1,3,4-triphenylcyclopentanols (**2**), *meso*- and (±)-1,3,4,6-tetraphenyl-1,6-hexanediones (**3**, **4**), as well as 5-benzoyl-1,3,4-triphenyl-1-penten-3-ol (**5**). All these products are derived from radical addition to a neutral CH molecule by CH anion radical (**7**) and CH ketyl radical formed in sequential electron transfer (from TEA to excited CH)–proton transfer (from $TEA^{\bullet+}$ to $CH^{\bullet-}$). Photoinduced reactions of **1a–1e** with *N,N*-dimethylaniline (DMA) afforded, in addition to the hydrodimerization products **2–5**, a CH–DMA addition product **16** formed by radical combination of CH ketyl –*N*-methyl-*N*-phenylaminomethyl radical pairs. The yield of **16** and the product ratio (addition-to-hydrodimerization ratio *A/H*) are affected by amine structures and reaction conditions. Therefore an increase in solvent polarity in the order benzene–acetonitrile–methanol and the presence of anhydrous magnesium perchlorate (special salt effect) result in decreases in the yield of **16** and in the ratio *A/H* by inhibiting in-cage proton transfer and promoting ion pair dissociation. An electron-withdrawing substituent at the benzene ring of DMA increases the yield of **16** and the *A/H* ratio by enhancing proton transfer from $DMA^{\bullet+}$ to $CH^{\bullet-}$, while a donor substituent on DMA has the reverse effect.

Keywords: Photoinduced reduction; Chalcone derivatives; Amines

1. Introduction

Photoinduced reduction reactions of ketones in the presence of amines have been under active research in recent years and have contributed a substantial amount of knowledge on many mechanistic aspects of photoinduced electron transfer (SET) reactions such as the different reactive intermediates involved in SET process and the factors that influence their reactivities in subsequent reactions [1]. Cookson et al. [2] first reported the photoinduced reductions of α,β-unsaturated carbonyl compounds in the presence of amines in 1968. Later, photoinduced reductions of cyclic enones, especially cyclohexenone and its derivatives have been intensively researched from the mechanistic and synthetic aspects [3–5]. These reactions have proven to be more intricate in reaction modes and mechanisms than those of simple ketones. Many mechanistic details have been clarified and it has been shown that basicity of enone anion radicals, thermodynamic and kinetic acidities of the amine cation radicals, and other factors that influence ion pair formation, such as solvent polarity, are of crucial importance in determining the SET efficiency and governing the further reaction pathways of the initially formed ion radical pairs. Synthetic methodology has also been evolved from these enone–amine photoreactions, especially in the intramolecular cyclizations by the use of α-silylamines [4,5b].

Photoinduced reactions of acyclic, α,β-unsaturated carbonyl compounds with amines, on the contrary, have not been as widely investigated as their cyclic counterparts [2] although diversified reaction modes and mechanisms, as well as differences in these respects from that of cyclic enones, can be anticipated considering the wide varieties of possible structures around the conjugated C=O and C=C double bonds and their influences on the properties of the excited states and of the anion radicals formed in SET process. In response to this situation, we report here the photoinduced reactions of chalcone (CH) derivatives **1a–1e** with amines. Another reason in choosing CH for investigation is that, although thermal reduction of CH derivatives has long been actively investigated under different conditions (such as in the presence of zinc [6], potassium [7], Cr(III) [8], Co(II) [9], anthracene hydride [10], rare earth metals (Yb and Os)

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Table 1
Photoinduced reactions of chalcones 1a–1e with TEA [a]

Enone	Solvent	Irradiation time (h)	Conversion (%)	Product (yield [b] (%))
1a	MeCN	11	96	2a (17), 3a (34), 4a (15), 5a (29)
1a	C_6H_6	11.5	91	2a (30), 3a (21), 4a (3), 5a (35)
1b	MeCN	11.5	96	2b (18), 3b (27), 4b (18), 5b (37)
1c	MeCN	11	94	2c (13), 3c (25), 4c (22), 5c (34)
1d	MeCN	11.5	89	2d (25), 3d (20), 4d (14), 5d (21)
1e	MeCN	11.5	100	2e (16), 3e (21), 5e (26), 6e (10)

[a] [enone], 0.1 M; [TEA], 0.5 M.
[b] Yield based on consumed chalcones.

and their salts [11,12], and in electrolytic reductions [13]), many problems regarding possible reaction modes and mechanisms in these reactions need to be further clarified. It is therefore highly desirable to see the results of photoinduced reductions of CH to shed new light in these respects.

2. Experimental details

Melting points were determined on a microscopic apparatus and are reported uncorrected. IR spectra were recorded on a Shimadzu IR-408 or a Nicolet FTIR 5DX spectrometer with KBr pellets.

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL PMX60 SI or a Bruker AM-500 spectrometer with Me_4Si as internal standard. Mass spectroscopy (MS) was carried out on a VG ZAB HS spectrometer. The elemental analyses were done with a Perkin–Elmer 240-C instrument.

Benzene (A.R. grade) was dried with sodium and distilled before use. Acetonitrile (C.P. grade) was refluxed with P_2O_5 for 2 h and distilled; then it was refluxed with anhydrous potassium carbonate for 2 h and redistilled. Triethylamine (TEA) was dried with and then distilled from sodium. *N,N*-Dimethylaniline (DMA) was dried with anhydrous KOH and distilled before use. *N,N*-dimethyltoluidine (DMT) and 4-chloro-*N,N*-dimethylaniline (CDMA) were prepared by literature procedures [14]. The chalcones **1a–1e** were prepared by condensation of benzaldehydes with the corresponding acetophenone [15].

The light source is a 500 W medium pressure mercury vapour lamp in a glass water-cooled jacket which cuts off light shorter than about 300 nm. The solutions were placed in glass tubes surrounding the light source to be photolysed with continuous dry argon purging.

2.1. Preparative photolyses of chalcones with the amines

The general procedures used for the preparative photolyses are as follows. MeCN or benzene solutions of the appropriate chalcone and the amine were irradiated and thin layer chromatography was used to monitor the reactions. The photolysate was then rotary evaporated and the residue subjected to chromatographic separation on a silica gel column with petroleum ether (boiling point (b.p.), 60–90 °C)–ethyl acetate as eluents to give the products with yields listed in Tables 1 and 2.

Table 2
Photoinduced reactions of chalcones 1a–1e in the presence of *N,N*-dimethylarylamines

Enone	Amine	pK_a of amine$^{\cdot+}$	Solvent	Irradiation time (h)	Conversion (%)	Product (yield [a] (%))	*A/H* [b]
1a	DMA	9	C_6H_6	11.5	93	2a (12), 3a (2), 5a (8), 16a (54)	2.45
1a	DMA	9	CH_3CN	11.5	91	2a (17), 3a (14), 4a (1), 5a (28), 16a (32)	0.52
1a	DMA	9	MeOH	13	92	2a (17), 3a (14), 4a (1), 5a (15), 16a (26)	0.40
1a	DMA	9	MeCN, $Mg(ClO_4)_2$ (0.1 M)	12	82	2a (25), 3a (27), 5a (7), 16a (15)	0.25
1a	DMT	12	C_6H_6	12.5	95	2a (20), 5a (26), 17 (30)	0.66
1a	CDMA	9	C_6H_6	15	92	2a (18), 5a (5), 18 (57)	2.52
1b	DMA	9	MeCN	11.5	94	2b (20), 3b (13), 4b (6), 5b (23), 16b (25)	0.42
1c	DMA	9	MeCN	11.5	91	2c (19), 3c (7), 4c (3), 5c (16), 16c (30)	0.67
1d	DMA	9	MeCN	14	93	2d (24), 3d (8), 5d (17), 16d (34)	0.70
1e	DMA	9	MeCN	12.3	93	2e (14), 3e (4), 5e (11), 6 (6), 16e (38)	1.10

[a] Yields based on consumed chalcones.
[b] *A/H* = (yield of addition product)/[total yield of hydrodimerization products (2–5)].

2.1.1. Irradiation of chalcones 1a–1e with triethylamine

These were as follows.

(1) *In benzene.* A solution of **1a** (1.04 g, 5 mmol) and TEA (2.5 g, 25 mmol) in benzene (50 ml) was irradiated for 11.5 h. The precipitated solid product **3a** (285 mg (30%)) was separated by filtration and washed with small portions of acetone. The combined washings and photolysate were concentrated in vacuo and the residue was chromatographically separated on a silica gel column to afford unreacted **1a** (90 mg (a conversion of 91%)), products **2a** (195 mg (21%)), **4a** (30 mg (3%)) and **5a** (335 mg (35%)).

(2) *In acetonitrile.* A solution of **1c** (1.04 g, 5 mmol) and TEA (2.5 g, 25 mmol) in MeCN (50 ml) was irradiated for 11 h. The photolysate was worked up as above to afford unreacted **1a** (40 mg (a conversion of 96%)), **2a** (170 mg (17%)), **3a** (335 mg (34%)), **4a** (150 mg (15%)) and **5a** (285 mg (29%)).

A solution of **1b** (1.11 g, 5 mmol) and TEA (2.5 g, 25 mmol) in MeCN (50 ml) was irradiated for 11.5 h to give unreacted **1b** (50 mg (a conversion of 96%)), **2b** (195 mg (18%)), **3b** (290 mg (27%)), **4b** (185 mg (18%)) and **5b** (390 mg (37%)).

A solution of **1c** (1.13 g, 5 mmol) and TEA (2.5 g, 25 mmol) in MeCN (50 ml) was photolysed for 11 h to give unreacted **1c** (70 mg (a conversion of 94%)), **2c** (135 mg (13%)), **3c** (265 mg (25%)), **4c** (235 mg (22%)) and **5c** (360 mg (34%)).

A solution of **1d** (1.26 g, 5 mmol) and TEA (2.5 g, 25 mmol) in MeCN (50 ml) was photolysed for 12.5 h to give unreacted **1d** (140 mg (89% conversion)), **2d** (280 mg (25%)), **3d** (225 mg (20%)), **4d** (160 mg (14%)) and **5d** (235 mg (21%)).

A solution of **1e** (1.21 g, 5 mmol) and TEA (2.5 g, 25 mmol) in acetonitrile (50 ml) was photolysed for 12.5 h to give **2e** (197 mg (16%)), **3e** (255 mg (21%)), **5e** (310 mg (26%)) and **6** (115 mg (10%)).

2.1.2. Irradiation of chalcones 1a–1e with N,N-dimethylanilines

These were as follows.

(1) *In benzene.* A solution of **1a** (1.04 g, 5 mmol) and DMA (1.21 g, 10 mmol) in benzene was photolysed for 11.5 h to give unreacted **1a** (70 mg (a conversion of 93%)), **2a** (115 mg (12%)), **5a** (80 mg (8%)) and **16a** (835 mg (54%)).

A solution of **1a** (0.84 g, 4 mmol) and DMT (1.08 g, 8 mmol) in benzene (40 ml) was photolysed for 12.5 h to give unreacted **1a** (40 mg (a conversion of 95%)), **2a** (160 mg (20%)), **5a** (205 mg (26%)) and **17** (395 mg (30%)).

A solution of **1a** (0.84 g, 4 mmol) and CDMA (1.25 g, 8 mmol) in benzene (40 ml) was photolysed for 15 h to give unreacted **1a** (70 mg (a conversion of 92%)), **2a** (135 mg (18%)), **5a** (40 mg (5%)) and **18** (770 mg (57%)).

(2) *In acetonitrile.* A solution of **1a** (1.04 g, 5 mmol) and DMA (3 g, 25 mmol) in MeCN (50 ml) was photolysed for 11.5 h to give unreacted **1a** (90 mg (a conversion of 91%)), **2a** (165 mg (17%)), **3a** (130 mg (13.7%)), **4a** (10 mg (1%)), **5a** (270 mg (28%)) and **16a** (475 mg (32%)).

A solution of **1b** (1.11 g, 5 mmol) and DMA (3 g, 25 mmol) in acetonitrile (50 ml) was photolysed for 11.5 h to give unreacted **1b** (70 mg (a conversion of 94%)), **2b** (205 mg (20%)), **3b** (135 mg (13%)), **4b** (60 mg (6%)), **5b** (235 mg (23%)) and **16b** (415 mg (25%)).

A solution of **1c** (0.668 g, 3 mmol) and DMA (1.81 g, 15 mmol) in MeCN (30 ml) was photolysed for 11.5 h to give unreacted **1c** (60 mg (a conversion of 91%)), **2c** (115 mg (19%)), **3c** (45 mg (7%)), **4c** (20 mg (3%)), **5c** (95 mg (16%)) and **16c** (305 mg (30%)).

A solution of **1d** (1.26 g, 5 mmol) and DMA (3 g, 25 mmol) in MeCN (50 ml) was photolysed for 14 h to give unreacted **1d** (95 mg (a conversion of 93%)), **2d** (275 mg (24%)), **3d** (98 mg (8%)), **5d** (192 mg (17%)) and **16d** (585 mg (34%)).

A solution of **1e** (1.21 g, 5 mmol) and DMA (3 g, 25 mmol) in MeCN (50 ml) was photolysed for 12.3 h to give unreacted **1e** (90 mg (a conversion of 92.6%)), **2e** (115 mg (14%)), **3e** (45 mg (4%)), **5e** (120 mg (11%)), **6** (65 mg (6%)) and **16e** (635 mg (38%)).

An MeCN solution (50 ml) containing **1a** (1.04 g, 5 mmol), DMA (3 g, 25 mmol) and anhydrous magnesium perchlorate $Mg(ClO_4)_2$ (1.12 g, 5 mmol) was photolysed for 12 h. The precipitated solid product **3a** (230 mg (27%)) was filtered out and washed with small portions of acetone. The combined washings and photolysate was concentrated in vacuo to about one third of the original volume. The residue was mixed with water (50 ml) and was then extracted with chloroform (3 × 20 ml). The combined chloroform solution was washed with water (2 × 30 ml) and dried with anhydrous magnesium sulphate and concentrated in vacuo. The residue was chromatographed on a silica gel column to give unreacted **1a** (190 mg (a conversion of 82%)), **2a** (210 mg (25%)), **5a** (60 mg (7%)) and **16a** (200 mg (15%)).

(3) *In methanol.* A solution of **1a** (1.04 g, 5 mmol) and DMA (3 g, 25 mmol) in newly distilled methanol (50 ml) was photolysed for 13 h to give unreacted **1a** (95 mg (a conversion of 93%)), **2a** (230 mg (24%)), **4a** (40 mg (4%)), **5a** (140 mg (15%)) and **16a** (60 mg (24%)).

2.2. Irradiation of 1a with N-methylaniline

A solution of **1a** (1.04 g, 5 mmol) and *N*-methylaniline (2.5 g, 23.6 mmol) in benzene (50 ml) was photolysed for 18 h. Work-up of the photolysate as described above gave unreacted **1a** (240 mg (a conversion of 77%)), **2a** (420 mg (53%)), **3a** (20 mg (3%)), **5a** (60 mg (8%)) and **8** (270 mg (34%)).

1*R, 2*S**, 3*R**, 4*S**-1-Phenyl-1-(2-hydroxy-2,4,5-triphenylcyclopentyl)methanone (2a):** Melting point (m.p.), 197–198 °C (196–198 °C [6b]). IR: ν_{max} 3380 (OH), 1628, 1585, 1480, 1438, 1380, 1238, 745 and 695 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.517 (1H, q, J = 5.52, 13.71 Hz), 2.929 (1H, t, J = 13.71 Hz), 3.713 (1H, ddd, J = 13.71,

11.46, 5.52 Hz), 4.035 (1H, t, J = 11.46 Hz), 4.466 (1H, d, J = 11.46 Hz), 5.178 (1H, s), 6.96–7.51 (20H, m, ArH ppm). MS: m/z 400 ($M^+ - H_2O$, 13.1), 105 ($PhCO^+$, base).

***meso*-1,3,4,6-Tetraphenyl-1,6-hexanedione (3a)**: M.p., 267–268 °C (270 °C [6b]). IR: ν_{max} 3100, 3080, 3035, 1678, 1598, 1580, 1498, 1450, 1242, 980, 758, 710, 700 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 2.902 (1H, d, J = 16.6 Hz), 3.145 (2H, dd, J = 16.6, 9.6 Hz), 3.941 (2H, d, J = 9.6 Hz), 6.84–7.55 (20H, m, ArH) ppm. MS: m/z 400 ($M^+ - H_2O$, 5.1), 298 (18), 295 (18), 209 (6.6), 105 (base).

(±)1,3,4,6-Tetraphenyl-1,6-hexanedione (4a): M.p. 179–181 °C. IR: ν_{max} 3015, 1671, 1590, 1571, 1489, 1445, 1234, 980, 738, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.391 (4H, d, J = 5.7 Hz), 3.86 (2H, t, J = 5.7 Hz), 6.95–7.85 (20H, m, ArH) ppm. MS: m/z 400 ($M^+ - H_2O$, 3.4), 298 (29.3), 209 (16.7), 105 (base). Anal. Found: C, 86.30; H, 6.119. $C_{30}H_{26}O_2$ calc.: C, 86.09; H, 6.261%.

4-Hydroxy-1,3,4,5-tetraphenyl-5-hexen-1-one (5a): M.p., 154–156 °C. IR: ν_{max} 3450, 1640, 1598, 1580, 1493, 1450, 1390, 1250, 750, 695 cm^{-1}. ^1H NMR (CCl_4, 500 MHz): δ 2.28 (1H, s, OH), 3.20 (1H, dd, J = 17.4, 5.6 Hz), 3.745 (1H, dd, J = 17.4, 6.3 Hz), 4.164 (1H, dd, J = 6.3, 5.6 Hz), 6.556 (1H, d, J = 15.82 Hz, CH=), 6.634 (1H, d, J = 15.82 Hz, CH=), 6.9–7.8 (20H, m, ArH) ppm. MS: m/z 400 ($M^+ - H_2O$, 8.2), 295 (29.0), 209 (23.4), 105 (base). Anal. Found: C, 85.94; H, 6.250. $C_{36}H_{26}O_2$ calc.: C, 86.09; H, 6.261%.

1*R, 2*S**, 3*R**, 4*S**-1-Phenyl-1-(2-hydroxy-2-phenyl-4,5-di(*p*-tolyl)cyclopentyl)methanone (2b)**: M.p. 206–207 °C. IR: ν_{max} 3410, 1635, 1592, 1578, 1512, 1446, 1375, 1244, 1042, 812, 758, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.160 (3H, s, CH_3), 2.280 (3H, s, CH_3), 2.538 (1H, dd, J = 6.1, 14.7 Hz), 2.971 (1H, dd, J = 10.9, 14.7 Hz), 3.717 (1H, ddd, J = 11.35, 10.92, 6.10 Hz), 4.057 (1H, t, J = 11.35 Hz), 4.493 (1H, d, J = 11.35 Hz), 5.13 (1H, s, OH), 6.88–7.57 (18H, m, ArH) ppm. MS: m/z 446 (M^+, 1.7), 428 ($M^+ - H_2O$ 5.4), 309 (96.1), 223 (67.7), 165 (29.4), 105 (base). Anal. Found: C, 85.64; H, 6.940. $C_{32}H_{30}O_2$ calc.: C, 86.06; H, 6.771%.

***meso*-1,6-Diphenyl-3,4-di(*p*-tolyl)-1,6-hexanedione (3b)**: M.p., 260–261 °C. IR: ν_{max} 3080, 3040, 3020, 1680, 1600, 1580, 1448, 1375, 1280, 1238, 975, 835, 762, 692 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 2.152 (6H, s, $2CH_3$), 3.072 (2H, d, J = 16.3 Hz), 3.312 (2H, dd, J = 16.3, 8.9 Hz), 4.059 (2H, d, J = 8.9 Hz), 6.96–7.70 (18H, m, ArH) ppm. MS: m/z 428 ($M^+ - H_2O$, 2.9), 326 (80.7), 223 (12.6), 105 (base). Anal. Found: C, 85.68; H, 7.059. $C_{32}H_{30}O_2$ calc.: C, 86.06; H, 6.771%.

(±)1,6-Diphenyl-3,4-di(*p*-tolyl)-1,6-hexanedione (4b): M.p., 176–178 °C. IR: ν_{max} 1672, 1588, 1570, 1508, 1443, 1355, 1215, 1015, 805, 746, 680 cm^{-1}. ^1H NMR ($(CD_3)_2SO$, 500 MHz): δ 2.262 (6H, S, $2CH_3$), 3.29–3.39 (4H, m), 3.81–3.84 (2H, m) 6.862 (4H, d, J = 7.73 Hz), 6.976 (4H, d, J = 7.73 Hz), 7.389 (4H, t, J = 7.56 Hz), 7.504 (2H, t, J = 7.56 Hz), 7.831 (4H, d, J = 7.56 Hz) ppm. MS: m/z 446 (M^+, 0.2) 428 ($M^+ - H_2O$, 3.3), 326 (67.5), 223 (64.4), 105 (base). Anal. Found: C, 85.92; H, 6.933. $C_{32}H_{30}O_2$ calc. C, 86.06; H, 6.771%.

4-Hydroxy-3,6-di(*p*-tolyl)-3,4-diphenyl-5-hexen-1-one (5b): M.p., 159–161 °C. IR: ν_{max} 3500, 1654, 1586, 1570, 1502, 1440, 1363, 1260, 1216, 796, 746, 698, 685 cm^{-1}. ^1H NMR (CCl_4, 500 MHz): δ 2.326 (1H, s, OH), 2.390 (3H, s, CH_3), 2.502 (3H, s, CH_3), 3.351 (1H, dd, J = 17.3, 6.2 Hz), 3.857 (1H, dd, J = 17.3, 6.2 Hz), 4.290 (1H, t, J = 6.2 Hz), 6.686 (1H, d, J = 15.6 Hz, CH=), 6.759 (1H, d, J = 15.6 Hz, =CH), 6.96–7.98 (18H, m, ArH) ppm. MS: m/z 429 ($M^+ - OH$, 5.7), 325 (27.4), 126 (49.9), 105 (28.5), 91 (base). Anal. Found: C, 85.12; H, 6.703. $C_{32}H_{30}O_2$ calc.: C, 86.06; H, 6.771%.

1*R, 2*S**, 3*R**, 4*S**-1-Phenyl-1-[2-hydroxy-2-phenyl-4,5-di(4-fluorophenyl)cyclopentyl]methanone (2c)**: M.p. 174–176 °C. IR: ν_{max} 3490, 1670, 1640, 1600, 1580, 1512, 1232, 1162, 840, 764, 710 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.514 (1H, d, J = 14.48, 5.87 Hz), 2.976 (1H, dd, J = 14.48, 11.52 Hz), 3.674 (1H, ddd, J = 11.52, 11.52, 5.87 Hz), 4.014 (1H, dd, J = 11.52 Hz), 4.486 (1H, d, J = 11.52 Hz), 5.207 (1H, s, OH), 6.78–7.56 (18H, m, ArH) ppm. MS: m/z 436 ($M^+ - H_2O$, 15.9), 331 (21.6), 327 (14.1), 105 (base). Anal. Found: C, 78.84; H, 5.188. $C_{30}H_{24}F_2O_2$ calc.: C, 79.24; H, 5.322%.

***meso*-1,6-Diphenyl-3,4-di(4-fluorophenyl)-1,6-hexanedione (3c)**: M.p., 252–253 °C. IR: ν_{max} 3080, 3050, 3020, 1678, 1600, 1580, 1508, 1372, 1282, 1224, 1158, 978, 842, 762, 736, 718, 695 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 2.86 (2H, d, J = 16.7 Hz), 3.02 (2H, dd, J = 16.7, 7.9 Hz), 3.80 (2H, d, J = 7.9 Hz), 6.78–7.61 (18H, m, ArH) ppm. MS: m/z 436 ($M^+ - H_2O$, 11.3), 334 (14.5), 331 (16.9), 105 (base). Anal. Found: C, 78.97; H, 5.128. $C_{30}H_{24}F_2O_2$ calc.: C, 79.24; H, 5.322%.

(±)1,6-Diphenyl-3,4-di(4-fluorophenyl)-1,6-hexanedione (4c): M.p., 151–152 °C. IR: ν_{max} 1670, 1595, 1504, 1442, 1220, 1154, 812, 754, 724, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.357 (4H, d, J = 5.64 Hz), 3.809 (2H, t, J = 5.64 Hz), 6.80–7.86 (18H, m, ArH) ppm. MS: m/z 454 (M^+, <0.1), 436 ($M^+ - H_2O$, 3.3), 334 (12.0), 227 (20.7), 105 (base). Anal. Found: C, 78.97; H, 5.128. $C_{30}H_{24}F_2O_2$ calc.: C, 79.24; H, 5.322%.

4-Hydroxy-3,6-di(4-fluorophenyl)-1,4-diphenyl-5-hexen-1-one (5c): M.p., 134–136 °C. IR: ν_{max} 3500, 1668, 1600, 1582, 1512, 1452, 1221, 1164, 856, 820, 761, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.293 (1H, s, OH), 3.388 (1H, dd, J = 17.5, 7.3 Hz), 3.729 (1H, dd, J = 17.5, 5.4 Hz), 4.147 (1H, dd, J = 7.3, 5.4 Hz), 6.599 (1H, d, J = 16.4 Hz, CH=), 6.673 (1H, d, J = 16.4 Hz, CH=), 6.75–7.85 (18H, m, ArH) ppm. MS: m/z 436 ($M^+ - H_2O$, 6.0), 331 (51.6), 209 (12.0), 109 (22.1), 105 (base). Anal. Found: C, 78.97; H, 5.128. $C_{30}H_{24}F_2O_2$ calc.: C, 79.24; H, 5.322%.

1*R, 2*S**, 3*R**, 4*S**-1-Phenyl-1-[2-hydroxy-2-phenyl-4,5-di(3,4-methylenedioxyphenyl)cyclopentyl]methanone (2d)**: M.p., 201–203 °C. IR: ν_{max} 3450, 2875, 1664,

1640, 1592, 1500, 1485, 1445, 1380, 1250, 1100, 1043, 935, 866, 812, 760, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.458 (1H, dd, J = 13.83, 6.14 Hz), 2.923 (1H, dd, J = 13.83, 11.64 Hz). 3.597 (1H, ddd, J = 11.55, 11.64, 6.14 Hz), 3.950 (1H, t, J = 11.55 Hz), 4.415 (1H, d, J = 11.55 Hz), 5.152 (1H, s, OH), 5.804 (1H, s, $\frac{1}{2}$O–CH_2–O), 5.812 (1H, s, $\frac{1}{2}$O–CH_2–O), 5.902 (2H, s, –O–CH_2–O–), 6.51–7.54 (16H, m, ArH) ppm. MS: m/z 506 (M^+, 0.2), 488 (4.9), 386 (10.0), 253 (14.8), 105 (base). Anal. Found: C, 75.77; H, 5.390. $C_{32}H_{26}O_6$ calc.: C, 75.88; H, 5.173%.

***meso*-1,6-Diphenyl-3,4-di(3,4-methylenedioxyphenyl)-1,6-hexanedione (3d)**: M.p., 280–282 °C. IR: ν_{max} 1670, 1593, 1500, 1485, 1441, 1364, 1250, 1195, 1100, 1048, 940, 810, 762, 740, 680 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz): δ 2.846 (2H, d, J = 15.31 Hz), 3.57–3.65 (4H, m), 6.022 (2H, s, –O–CH_2–O–), 6.044 (2H, s, –O–CH_2–O–), 6.64–7.85 (16H, m, ArH) ppm. MS: m/z 505 ($M^+ - 1$, <0.1), 488 ($M^+ - H_2O$, 0.8), 386 (10.2), 253 ($\frac{1}{2}M^+$, 5.1) 105 (base). Anal. Found: C, 75.80; H, 5.008. $C_{32}H_{26}O_6$ calc.: C, 75.88; H, 5.173%.

(±)1,6-Diphenyl-3,4-di(3,4-methylenedioxyphenyl)-1,6-hexanedione (4d): M.p., 182–184 °C. IR: ν_{max} 1660, 1592, 1500, 1486, 1440, 1360, 1300, 1250, 1100, 1040, 960, 928, 818, 798, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.88 (4H), 4.41 (2H), 5.98 (2H, s), 5.92 (2H, s), 6.66–7.70 (16H, m, ArH) ppm. MS: m/z 488 ($M^+ - H_2O$, 24.5), 386 (2.4), 384 (20.1), 383 (73.0), 253 (5.9), 135 (45.4), 105 (base). Anal. Found: C, 75.43; H, 5.206. $C_{32}H_{26}O_6$ calc.: C, 75.88; H, 5.173%.

4-Hydroxy-1,4-diphenyl-3,6-di(3,4-methylenedioxyphenyl)-5-hexen-1-one (5d): M.p., 144–145 °C. IR: ν_{max} 3500, 1668, 1594, 1579, 1500, 1481, 1440, 1360, 1250, 1185, 1155, 1100, 1035, 980, 928, 910, 863, 805, 768, 754, 740, 700 cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 500 MHz): δ 3.32 (1H, s, OH), 3.667 (2H, m), 4.011 (1H, t), 5.796 (1H, s, $\frac{1}{2}$O–CH_2–O–), 5.820 (1H, s, $\frac{1}{2}$O–CH_2–O–), 5.963 (2H, s, –OCH_2–O–) 6.461 (1H, d, J = 7.88 Hz, CH=), 6.572 (1H, d, J = 7.88 Hz, =CH), 6.64–7.93 (16H, m, ArH) ppm. MS: m/z 488 (14.4), 384 (5.3), 383 (57.0), 368 (19.8), 353 (27.2), 252 (18.7), 135 (39.0), 105 (base). Anal. Found: C, 76.01; H, 5.138. $C_{32}H_{26}O_6$ calc.: C, 75.88; H, 5.173%.

1*R, 2*S**, 3*R**, 4*S**-1-(4-Chlorophenyl)-1-[2-hydroxy-2-(4-chlorophenyl)-4,5-diphenylcyclopentyl]methanone (2e)**: M.p., 179–181 °C. IR: ν_{max} 3450, 1645, 1592, 1490, 1402, 1378, 1245, 1180, 1092, 1052, 1010, 850, 830, 770, 741, 709 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.559 (1H, dd, J = 14.38, 5.26 Hz), 2.913 (1H, t, J = 14.33 Hz), 3.789 (1H, ddd, J = 14.33, 5.26, 11.46 Hz), 4.065 (1H, t, J = 11.46 Hz), 4.393 (1H, d, J = 11.46 Hz), 5.293 (1H, s, OH), 7.05–7.50 (18H, m, ArH) ppm. MS: m/z 486 (M^+, 0.1), 468 ($M^+ - H_2O$, 7.1), 332 (21.3), 243 (53.8), 141 (38.2), 139 (base). Anal. Found: C, 74.01; H, 4.921. $C_{30}H_{24}O_2Cl_2$ calc.: C, 73.93; H, 4.963%.

***meso*-3,4-Diphenyl-1,6-di(*p*-chlorophenyl)-1,6-hexanedione (3e)**: M.p., 243–244 °C. IR: ν_{max} 3070, 3035, 1682, 1592, 1495, 1400, 1230, 1088, 978, 824, 765, 706 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 2.875 (2H, d, J = 16.55 Hz), 3.105 (2H, dd, J = 16.55, 9.1 Hz), 3.989 (2H, d, J = 9.1 Hz), 6.91–7.46 (18H, m, ArH) ppm. MS: m/z 468 ($M^+ - H_2O$, 0.5), 332 (16.0), 243 (5.2), 141 (32.1), 139 (base). Anal. Found: C, 73.71; H, 4.799. $C_{30}H_{24}O_2Cl_2$ calc.: C, 73.93; H, 4.963%.

4-Hydroxy-1,4-di(4-chlorophenyl)-3,6-diphenyl-5-hexen-1-one (5e): M.p., 150–151 °C. IR: ν_{max} 3502, 1668, 1592, 1572, 1492, 1400, 1264, 1088, 992, 820, 758, 708 cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 500 MHz): δ 3.343 (1H, s, OH), 3.681 (1H, dd, J = 17.73, 8.67 Hz), 3.760 (1H, dd, J = 17.73, 4.22 Hz), 4.053 (1H, dd, J = 8.67, 4.22 Hz), 6.619 (1H, d, J = 15.91 Hz, CH=), 6.975 (1H, d, J = 15.91 Hz, =CH), 6.98–7.92 (18H, m, ArH) ppm. MS: m/z 468 ($M^+ - H_2O$, 10.1), 379 (12.2), 329 (64.4), 316 (20.1), 241 (17.5), 191 (21.1), 139 (base). Anal. Found: C, 74.20; H, 4.829. $C_{30}H_{24}O_2Cl_2$ calc.: C, 73.93; H, 4.963%.

1-Chlorophenyl-1-[2-hydroxy-2-(4-chlorophenyl)-4,5-diphenylcyclopentyl]methanone (6): M.p., 160–161 °C. IR: ν_{max} 3350, 1648, 1580, 1482, 1395, 1205, 1088, 820, 754, 688 cm^{-1}. ^1H NMR (C_6D_6, 500 MHz): δ 1.314 (1H, s, OH), 1.986 (1H, dd, J = 12.62, 5.65 Hz), 3.141 (t, J = 12.62 Hz), 4.015 (1H, ddd, J = 12.62, 10.18, 5.65 Hz), 4.193 (1H, dd, J = 10.18, 6.84 Hz), 4.507 (1H, d, J = 6.84 Hz), 6.78–7.50 (16H, m, ArH) ppm. MS: m/z 468 ($M^+ - H_2O$, 9.2), 377 (7.1), 332 (11.8), 329 (23.6), 243 (29.1), 139 (base). Anal. Found: C, 74.20; H, 4.994. $C_{30}H_{24}O_2Cl_2$ calc.: C, 73.93; H, 4.963%.

1-(3,4-diphenyl-2-benzoylcyclobut-1-yl)-1-phenyl methanone (8): M.p., 126 °C (126 °C [17]). IR: ν_{max} 1658, 1590, 1572, 1488, 1445, 1380, 1292, 1208, 1020, 770, 743 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 4.16 (2H, d, J = 9.0 Hz), 4.79 (2H, d, J = 9.0 Hz), 7.37–8.17 (20H, m, ArH) ppm. MS: m/z 416 (M^+, 1.1), 311 (24.5), 208 (90.1), 105 (base).

4-(*N*-Methyl-*N*-phenyl)amino-1,3-diphenyl-1-butanone (16a): M.p., 108–109 °C. IR: ν_{max} 1680, 1595, 1568, 1512, 1450, 1380, 1362, 1351, 1276, 1222, 1004, 988, 743, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MH_2): see Fig. 1. MS: m/z 330 ($M^+ + 1$, 35.8) 329 (M^+, 4.5), 217 (60.8), 120 (39.5), 109 (39.2), 105 (23.5), 91 (base). Anal. Found: C, 83.47; H, 7.040. $C_{23}H_{23}NO$ calc.: C, 83.85; H, 7.040%.

4-(*N*-methyl-*N*-phenyl)-amino-1-phenyl-3-(4-tolyl)-1-butanone (16b): M.p., 78 °C. IR: ν_{max} 1671, 1591, 1500, 1443, 1368, 1192, 1108, 976, 804, 740, 680 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.45 (3H, s, CH_3), 2.83 (3H, s, CH_3), 3.3–4.2 (5H, m, –CH_2–CH–CH_2–), 6.6–8.2 (14H, m, ArH) ppm. MS: m/z 343 (M^+, 6.8), 223 (1.7), 120 (base). Anal. Found: C, 84.09, H, 7.620. $C_{24}H_{25}NO$ calc.: C, 83.93; H, 7.340%.

4-(*N*-Methyl-*N*-phenyl)amino-1-phenyl-3-(*p*-fluorophenyl)-1-butanone (16c): M.p., 86–87 °C. IR: ν_{max} 1668, 1598, 1500, 1442, 1368, 1339, 1268, 1212, 1152, 980, 968, 838, 812, 748, 737, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz), 2.76 (3H, s, CH_3), 3.2–4.2 (5H, m, –CH_2–CH–CH_2–), 6.6–8.2 (14H, m, ArH) ppm. MS: m/z 347 (M^+, 6.5), 227 (2.2),

120 (base). Anal. Found: C, 79.60; H, 6.045. $C_{23}H_{22}NOF$ calc.: C, 79.51; H, 6.380%.

4-(*N*-Methyl-*N*-phenyl)amino-1-phenyl-3-(3,4-methylenedioxy)phenyl-1-butanone (16d): M.p., 100–102 °C. IR: ν_{max} 1670, 1584, 1492, 1475, 1432, 1368, 1340, 1232, 1192, 1028, 983, 930, 860, 802, 736, 670 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.80 (3H, s, CH_3), 3.1–4.1 (5H, m, $-CH_2-CH-CH_2-$), 5.94 (2H, s, $-O-CH_2-O-$), 6.5–8.1 (13H, m, ArH) ppm. MS: m/z 373 (M^+, 2.4), 266 (0.8), 120 (base). Anal. Found: C, 77.09; H, 5.999. $C_{24}H_{23}NO_3$ calc.: C, 77.19; H, 6.208%.

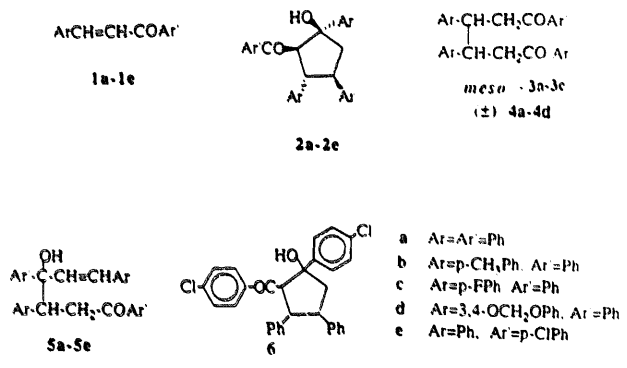
4-(*N*-Methyl-*N*-phenyl)amino-1-(*p*-chlorophenyl)-3-phenyl-1-butanone (16e): M.p., 104–106 °C. IR: ν_{max} 1671, 1595, 1580, 1502, 1375, 1356, 1345, 1212, 1091, 978, 812, 750, 734, 688 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz), 2.69 (3H, s, CH_3), 3.2–4.1 (5H, m, $-CH_2-CH-CH_2-$), 6.5–8.0 (14H, m, ArH) ppm. MS: m/z 363 (M^+, 1.1), 222 (13.9), 120 (base). Found: C, 76.04; H, 6.101. $C_{23}H_{22}NOCl$ calc.: C, 75.92; H, 6.094%.

4-[*N*-Methyl-*N*-(4-tolyl)]amino-1,3-diphenyl-1-butanone (17): M.p., 114–115 °C. IR: ν_{max} 1669, 1610, 1517, 1442, 1364, 1342, 1208, 1183, 790, 758, 736, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.21 (3H, s, CH_3), 2.61 (3H, s, CH_3), 3.1–4.1 (5H, m, $-CH_2CHCH_2-$), 6.4–7.9 (14H, m, ArH) ppm. MS: m/z 343 (M^+, 8.1), 223 (1.8), 134 (base). Anal. Found: C, 84.07; H, 7.249. $C_{24}H_{25}NOCl$ calc.: C, 83.93; H, 7.336%.

4-[*N*-Methyl-*N*-(*p*-chlorophenyl)]amino-1,3-diphenyl-1-butanone (18): Viscous oil. IR: ν_{max} 1670, 1590, 1496, 1443, 1368, 1340, 1228, 1195, 1012, 802, 742, 689 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.53 (3H, s, CH_3), 3.1–4.1 (5H, m, $-CH_2CHCH_2-$), 6.4–8.0 (14H, m, ArH) ppm. MS: m/z 363 (M^+, 0.3), 234 (7.9), 141 (6.3), 59 (base). Anal. Found: C, 76.21; H, 6.22. $C_{23}H_{22}NOCl$ calc.: C, 75.92; H, 6.10%.

3. Results and discussion

3.1. Photoinduced reactions of chalcones 1a–1e with triethylamine

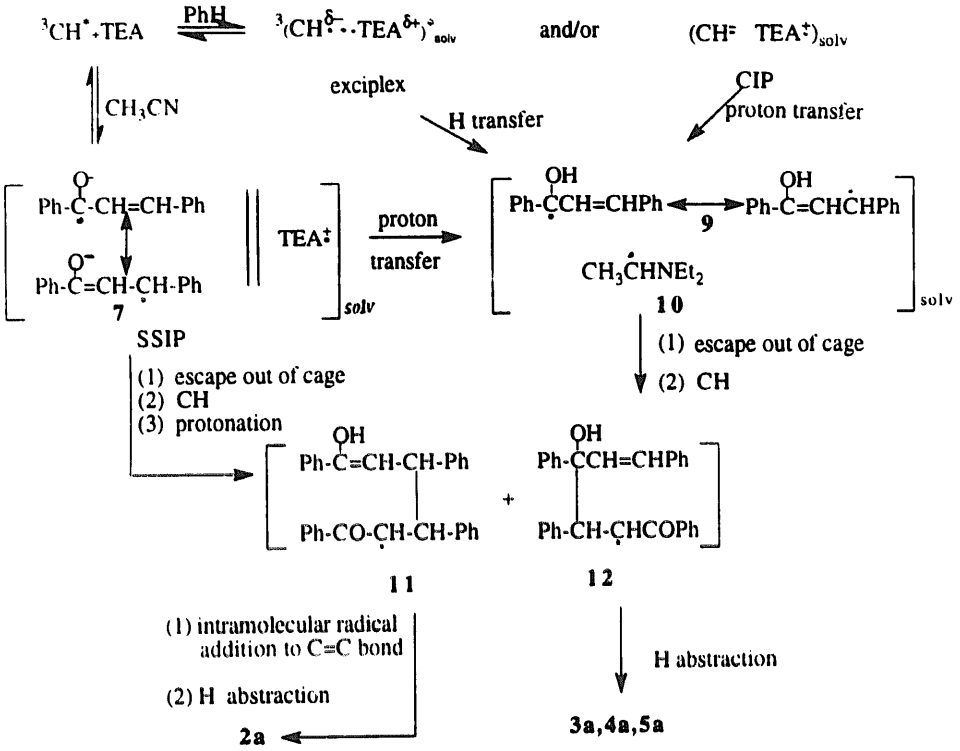


Irradiation of a solution of chalcone (CH) (**1a**) (0.1 M) and TEA (0.5 M) in acetonitrile for 11 h and subsequent careful chromatographic separation of the reaction mixture on a silica gel column afforded four products: **2a**, **3a**, **4a** and **5a**. The *cis*-2-benzoyl-1,3,4-triphenylcyclopentanol **2a** is formed with 17% yield. This product has previously been found in several thermal reduction reactions of CH [6–13], the structure of which had been proved by an X-ray crystallographic analysis [6b]. Products **3a** and **4a** are the *meso*- and (±)-1,3,4,6-tetraphenyl-1,6-hexanedione (34% and 15% yields) respectively. It is noted that, although the *meso*-diketone **3a** has also often been formed in thermal reductions of CH together with product **2a** [6–13], the (±)-diketone **4a** has not been found in any thermal reductions. The spectral data of **4a**, including major absorptions and their relative intensities in the IR spectrum, as well as fragmentations in mass spectrum are closely parallel to that for the *meso*-diketone **3a**. In contrast with **2a–4a** which are derived from $CH^{\bullet -}$ as a 1,4-anion radical, product **5a**, the 5-benzoyl-1,3,4-triphenyl-1-penten-3-ol, is derived from $CH^{\bullet -}$ with a 1,2-anion radical resonance structure. This product is also unknown in thermal reductions of CH where only products from $CH^{\bullet -}$ (**7** in Scheme 1) as 1,4-anion radical have been found, although electron paramagnetic resonance (EPR) studies and HMO calculation revealed that the β-carbon atom has comparable spin density with the carbonyl carbon atom in $CH^{\bullet -}$ [16], in line with our findings in the photoinduced reductions.

Photolyses of **1a** (0.1 M) with TEA (0.5 M) in benzene also gave products **2a–5a** (Table 1). Photoinduced reactions of chalcone derivatives **1b–1e** with TEA gave similar results as for **1a**. In each case except for **1e**, the corresponding products **2–5** are formed respectively. For **1e**, product **4e** is missing; instead, another cyclopentanol product **6**, which is a stereoisomer of product **2**, is obtained. The results are in Table 1.

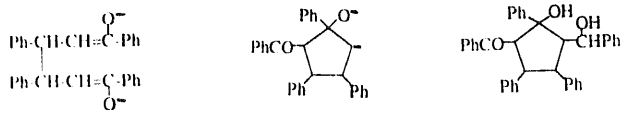
The characteristic feature of these photoinduced reductions of chalcone derivatives is that all the products are dihydrodimers derived from conjugate addition of CH ketyl to a CH molecule. The high reactivity of $CH^{\bullet -}$ for radical addition to a neutral CH molecule and the resulting short lifetime of $CH^{\bullet -}$ (**16a**) obviously suppressed other reaction pathways often found in photoreductions of cyclic enones, such as reduction to saturated ketone and ketyl radical coupling to pinacol products. It is also noted that products from radical addition of enone 1,2-anion radical to a neutral enone molecule as product **5** were not found in photoreductions of cyclic enones.

Chalcone has a T_1 state of π–π^* character [17]. Intersystem crossing of enone compounds is known to be very fast (about 10^{11} s^{-1}) with a unity quantum yield [18]. However, recent transient spectroscopic studies by Mataga and coworkers [19] and Peters and Lee [20] on photoinduced SET reactions of benzophenone (BP) with amines have shown that, when the amine concentrations are high (above 0.1 M), singlet BP may also be quenched by amine. In quenching studies with diazabicyclo[2.2.2]octane (DABCO) as electron donor, Peters and Lee showed that, at a DABCO concentration of 1 M, the excited BP quenched is 65% in triplet



Scheme 1.

and 35% in singlet [20]. In our present photoinduced reactions of CH with TEA (0.5 M), it is therefore assumed that, while triplet CH is the main species responsible for the reactions, singlet CH may also take part in the reactions.



13 14 15

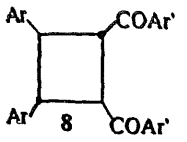
Starting from the CH T_1 state, the photoreductions may be initiated by two mechanisms: (1) hydrogen abstraction of ^{3}CH* from the TEA C_α–H bond leads directly to the formation of CH ketyl-α-aminoalkyl radical pair; (2) SET from TEA to ^{3}CH* and subsequent proton transfer from $TEA^{\bullet+}$ to $CH^{\bullet-}$ also gave the CH ketyl-α-aminoalkyl radical pair. Hydrogen abstraction reactions of CH triplet from hydrogen donor compounds have not been reported. Our own experiments show that prolonged irradiation of CH in hydrogen donor solvents i-PrOH and in toluene:benzene (1:3, v/v) resulted in slow consumptions of CH and gave only (2+2) cyclodimers of CH such as **8** [19]. Photoreduction products were not detected in these reactions. This behaviour of the T_1 state of CH is different from that of the T_1 (π–π^*) state of cyclohexenone derivatives which on photolyses in i-PrOH or toluene abstracts hydrogen at C_β to give cyclohexanones and radical coupling product 2-benzylcyclohexanone [21].

The lack of hydrogen abstraction ability of the CH T_1 state indicates that the photoinduced reductions of CH in the presence of TEA are not initiated by direct hydrogen abstraction of ^{3}CH* from the amine. On the contrary, photoinduced reductions of cyclic enones are known to proceed via a SET mechanism. Transient absorption spectroscopy studies [22] have shown that cyclohexenone has a twisted T_1(π–π^*) state with a lifetime of 23 ns and a triplet energy of 63 kcal mol^{-1}, which can be quenched by TEA in acetonitrile by SET process with a rate constant of 9×10^7 M^{-1} s^{-1} to give the enone anion radical–amine cation radical pair. This SET mechanism has also been proved by photo-CIDNP studies on photoinduced reactions between cyclohexenone and DABCO in acetonitrile [3b]. Triplet lifetime measurements by Caldwell and Singh [23] show that the T_1(π–π^*) states of chalcones are also twisted and have lifetimes similar to that of cyclohexenones. Since CH has no detectable phosphorescence at 77 K in EPA, the estimation of free energy change ΔG_{ET} for SET between ^{3}CA* and TEA by the Weller equation [24] is impeded by lack of accurate triplet energy value of CH. CH has a reduction potential of -1.48 V (saturated calomel electrode (SCE), CH_3CN) [7a] and is a stronger ground-state electron acceptor than cyclohexenone ($E_{1/2}^{red} = -2.15$ V (SCE, CH_3CN)) [25]. However, the triplet energy of CH is probably lower than that of cyclohexenone owing to the extended conjugation system and an increased structural flexibility toward twisting in CH. As a result, there is probably not much difference in the excited-state reduction potentials of the two. Furthermore, we have found that photolyses of **1a** in high oxidation potential tertiary "amines" such as *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide ($E_{1/2}^{ox} = 1.32$ V (SCE)) do not lead to photoreduction of CH. It is therefore proposed that these photoreductions are

initiated by SET process between triplet chalcones and TEA as shown in Scheme 1.

Transient spectroscopy studies on photoinduced SET reactions between ketones and amines by Peters and coworkers [26], Mataga and coworkers [19], Haselbach et al. [27] etc. and between *N*-phenyl-1,8-naphthalimide and amines by Berces and coworkers [28] have shown that photoinduced SET processes between triplet carbonyl compounds and amines lead to the formation of polar exciplexes and contact ion radical pairs (CIPs) in non-polar hydrocarbon solvents and the formation of solvent separated ion radical pairs (SSIPs) in acetonitrile. The SSIPs formed in CH_3CN also tend to dissociate further to give free ions. The pK_a value of the conjugate acid of enone anion radical (the ketyl radical) is in the range of about 10 in water [29]. Therefore the CH anion radical is basic enough to deprotonate the weakly acidic TEA cation radical ($pK_a \approx 8$ in water [30]) from its α-carbon atom. Hydrogen transfer in the exciplex and proton transfer in CIPs and SSIPs lead to the formation of enone ketyl (**9**)–α-aminoalkyl ($CH_3\dot{C}HNEt_2$) (**10**) radical pairs. Radical addition of CH ketyl (**7**) to the C=C double bond of a neutral CH molecule followed by disproportionation of the dimer radicals (**11,12**) with the aminoalkyl radical or by hydrogen abstraction of the dimer radical gave the diketone products **3** and **4**. The dimer radicals could alternatively undergo intramolecular cyclization to give the cyclopentanol products.

In thermal reductions of chalcone, products **2** and **3** have been proposed to be formed via dianion intermediates: (1) the radical coupling of two $CH^{\cdot -}$ gave the dianion **13** which can be protonated to give **3** or undergo intramolecular cyclization to give cyclopentanol dianion **14** which on protonation afforded **2**; (2) the dimer radical anion formed by addition of $CH^{\cdot -}$ with a neutral CH molecule can undergo intramolecular radical addition to give the cyclopentanol anion radical which on further reduction by metals also gave the dianion **14**. This mechanism has been proved in Yb-metal induced chalcone reductions by a trapping experiment in which the dianion is trapped by added benzaldehyde to give an addition product **15** [11b]. In the photoinduced reductions of CH in the presence of TEA, however, the dianion intermediates **13** and **14** could not be involved. Firstly this is because, in steady state photolyses, $CH^{\cdot -}$ cannot be formed in concentrations as large as in thermal reductions of CH by metals to allow any significant bimolecular radical coupling, leading the dianion to compete with other processes, as in cage proton transfer and $CH^{\cdot -}$ addition to neighbouring CH molecules present in large concentrations. Secondly, further reduction of cyclopentanol radical anion by TEA is thermodynamically unfavourable, considering that carbon-centred radicals usually have a reduction potential of about -1 V (SCE) [31] while the oxidation potential of TEA is 0.98 V (SCE) [32].



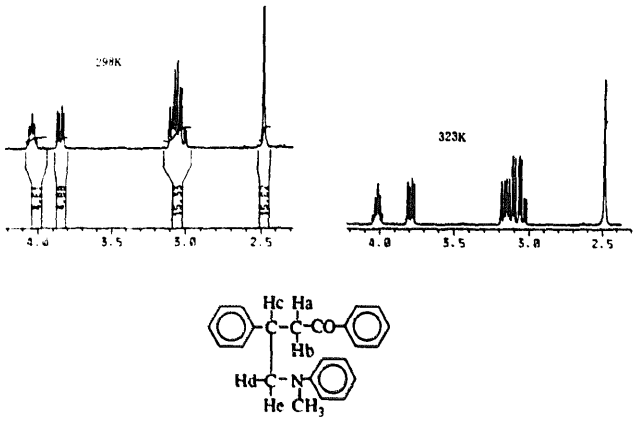


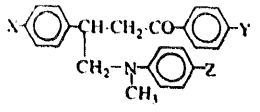
Fig. 1. ^{1}H NMR (500 MHz) of **16a**: (a) at room temperature (298 K); (b) at 323 K. (Only the region for aliphatic absorptions is shown.) H_a: δ 3.83 (dd, J_{ab} = 15.0 Hz, J_{ac} = 6.4 Hz). H_b: δ 3.10 (dd, J_{ba} = 15.0 Hz, J_{bc} = 8.7 Hz). H_c: δ 4.03 (dddd, J_{ca} = 6.4 Hz, J_{cb} = 8.7 Hz, J_{cd} = 7.1 Hz, J_{ce} = 5.9 Hz). H_d: δ 3.09 (dd, J_{dc} = 17.0 Hz, J_{de} = 7.1 Hz). H_e: δ 3.03 (dd, J_{ed} = 17.0 Hz, J_{ec} = 5.9 Hz).

3.2. *Photoinduced reactions of chalcones* **1a–1e** *with N,N-dimethylaniline*

Photolysis of CH (0.1 M) with DMA (0.5 M) in acetonitrile with light of wavelength greater than 300 nm gave, in addition to the hydrodimerization products **2a**, **3a**, **4a** and **5a**, a CH–DMA addition product **16a** with 32% yield.

In the room temperature (298 K) ^{1}H NMR spectrum of **16a**, the five aliphatic protons H_a–H_e all resonate in the range δ = 3–4 ppm and could not be resolved at 500 MHz frequency. However, when the temperature is raised to 323 K (50 °C), the resolution in the region of aliphatic absorptions is significantly improved (Fig. 1). At this temperature, routine ^{1}H NMR (500 MHz) combined with a decoupling experiment by irradiating H_e and a C–H COSY allows complete assignment of the absorptions for H_a–H_e and the measurement of coupling constants between them to be made (Fig. 1).

Photolyses of chalcones **1b–1e** with DMA in CH_3CN gave results similar to **1a**.



16a X=Y=Z=H
16b X=CH_3,Y=Z=H
16c X=F,Y=Z=H
16d X=3,4-OCH_2O,Y=Z=H
16e X=Z=H,Y=Cl
17 X=Y=H,Z=CH_3
18 X=Y=H,Z=Cl

In all cases, addition products **16** are formed together with the hydrodimerization products. The results are in Table 2. The addition products **16a–16c** are formed by in-cage radical combination of the CH ketyl–α-aminoalkyl radic: pair after intersystem crossing to singlet manifold.

The photoinduced reactions of CH with *N*-methylaniline (NMA) were also investigated. Irradiation of a solution of CH (0.1 M) and NMA (0.46 M) in benzene led to the concomitant formation of the hydrodimerization products **2a** (53%), **3a** (3%), **5a** (8%) and the (2+2) cyclodimerization product **8** (34%). NMA has an oxidation potential of 1.03 V (SCE, CH_3CN) [32]. The rate of electron transfer

from NMA to ^{3}CH* is expected to be slower than that from DMA ($E_{1/2}^{ox}$ = 0.78 V (SCE)) or TEA ($E_{1/2}^{ox}$ = 0.98 V (SCE)), considering the less exergonic nature of the SET process. This is reflected in the longer irradiation time to bring about same conversions of CH in the reactions with NMA than with TEA or DMA. A decrease in SET rate constant makes the attack of ^{3}CH* to CH, leading to the (2+2) cyclodimerization product competitive with the ^{3}CH* quenching by NMA via SET, although the former process is very inefficient [17c].

To obtain more insight into the reaction mechanisms in the photoreductions of chalcones in the presence of amines, we have further investigated solvent polarity and special salt effects as well as the effects of the *para* substituents on the benzene ring in DMA on the reactions.

3.3. Solvent polarity and special salt effects on the reactions

It is found that the yields of DMA–CH addition product **16a** and the product ratio (addition-to-hydrodimerizations ratio *A*/*H* = (yield of **16a**)/(yield of **2–5**)) are dependent on solvent polarity (Table 2). The yield of **16a** is 54% in benzene (E_T = 34.3 [33]) and 32% in acetonitrile (E_T = 45.6). The *A*/*H* ratio is also higher in benzene (2.45) than in acetonitrile (0.52). Furthermore, when the photolysis of CH with DMA is carried out in methanol (E_T = 55.5; the Kamlet–Taft hydrogen bond donor acidity parameter α = 0.93 [34]), the yield of **16a** is found to be further decreased to 26%, and the *A*/*H* ratio is reduced to 0.40. These results reflected the importance of solvation on the forms and reactivities of the ion radical pairs formed in the initial SET process.

Investigations by Mataga and coworkers [19] on the dynamic properties of the ion radical pairs formed in photoinduced electron transfer between benzophenone (BP) and DMA showed that rate constant k_{PT} for in-cage proton transfer from DMA$^{\bullet+}$ to the ketone ketyl anion and the rate constant k_{ID} for ion radical pair dissociation are of comparable magnitude (5.4×10^9 M s^{-1} and 1.4×10^9 M^{-1} s^{-1} respectively). The competition between these two processes should therefore be sensitively affected by such factors as aminium radical acidity, ketyl anion basicity and solvent polarity. In the present case of photoinduced electron transfer between CH and DMA, in-cage proton transfer from DMA$^{\bullet+}$ to CH$^{\bullet-}$, which after intersystem crossing and radical pair combination leads to the formation of addition product, competes with ion radical pair dissociation which results in the attack of the free CH$^{\bullet-}$ to the neutral CH molecule in solution to give the hydrodimers. The yield of the addition product is therefore higher in benzene than in the polar acetonitrile which favours the further dissociation of the ion radical pairs. In protic solvents as methanol, the yield of addition product is further decreased because the hydrogen bonding interactions between the solvent and the oxyanion of CH$^{\bullet-}$ further diminish the basicity of CH$^{\bullet-}$ and inhibit the proton transfer from DMA$^{\bullet+}$ to CH$^{\bullet-}$, leading to a more efficient dissociation of the ion radical pairs.

A special salt effect [35] has recently been found to have a profound influence in photoinduced SET reactions on the dynamic behaviours [26b] of the ion radical pairs and on their further reaction pathways. Examples have been reported in photoinduced SET oxygenations and *cis*-, *trans*-isomerizations of small ring compounds [36] and in cyclohexenone–α-silylamine photo-SET reactions [37]. The addition of hard metal salts with anions of low nucleophilicity ($LiClO_4$, $LiBF_4$, $Mg(ClO_4)_2$ etc.) has the effects of inhibiting back electron transfer and promoting ion radical pair dissociation. The chemical consequence is a disturbance to the competition of in-cage and out-of-cage processes as reflected in the change in reaction product distributions. In the photoinduced reductions of chalcones with DMA, we have found that the addition of anhydrous magnesium perchlorate (0.1 M) into a CH (0.1 M)–DMA (0.25 M) solution in acetonitrile caused a drastic decrease in the yield of addition product **16a** and resulted in a change in *A*/*H* from 2.45 in benzene to 0.25 in acetonitrile (Table 2). This can be rationalized by the inhibition of proton transfer from DMA$^{\bullet+}$ to CH$^{\bullet-}$ by the shielding of the oxyanion in CH$^{\bullet-}$ by the Mg^{2+} ion.

3.4. Substituent effect on the photoinduced reactions of chalcones with dimethylaniline

Para substituents in the benzene ring of DMA also affect the (addition-to-hydrodimerization) product distributions. Photolysis of CH with *N*,*N*-dimethyltoluidine (DMT) in benzene led to a decreased yield of addition product **17** (30%) and a decreased *A*/*H* ratio (0.66) compared with the result for DMA (54% and 2.45 respectively). On the contrary, photolyses of CH with CDMA in benzene under the same conditions gave a slightly higher yield of the addition product **18** (57%) and a higher *A*/*H* ratio (2.52) (Table 2).

Parker and Tilset [38] have estimated the pK_a value of the cation radicals of the *para*-substituted *N*,*N*-dimethylanilines and measured the proton transfer rate constants k_{PT} from these cation radicals to acetate ion (conjugate acid; pK_a = 22) in acetonitrile using the derivative cyclic voltammetry technique. These results are included in Table 2. They found a linear correlation between the k_{PT} and the σ^+ value of the substituents with a ρ value of 1.67. The Brönsted plot of log k_{PT} vs. pK_a of the amine cation radicals yielded an α value of 0.24. Mariano and coworkers [39] generated the cation radicals of the *para*-substituted anilines by photoinduced SET to singlet-excited 1,4-dicyanobenzene and measured the bimolecular α-CH deprotonation rate constant k_{PT} of these tertiary aminium radicals by acetate ion in methanol:acetonitrile (6:4, v/v) solution with a time-resolved laser spectroscopy technique. A linear correlation between ln k_{PT} and the σ^+ value of the *para* substituents and a close relationship between the thermodynamic and kinetic acidities of the aminium ion radicals were also found. Proton transfer from DMT$^{\bullet+}$, DMA$^{\bullet+}$ and CDMA$^{\bullet+}$ to the acetate ion are

reported to have bimolecular rate constants k_{PT} of 1.1×10^8 $M^{-1}s^{-1}$, 6.2×10^8 $M^{-1}s^{-1}$ and 1×10^9 $M^{-1}s^{-1}$ respectively. Since the pK_a difference for the $DMA^{\cdot+}$–$CH^{\cdot-}$ system is smaller than for the ($DMA^{\cdot+}$–acetate ion) system, the k_{PT} value may be more sensitively dependent on the change in pK_a of the amine cation radicals for the substituted DMA–CH system than for the substituted DMA–acetate ion system (a later transition state for proton transfer and a larger α value for the former system). Proton transfer from $DMT^{\cdot+}$ to $CH^{\cdot-}$ and the formation of the CH ketyl–aminoalkyl radical pair, the precursor of the addition product, are therefore less feasible than for $DMA^{\cdot+}$. In contrast, proton transfer from $DMT^{\cdot+}$ to $CH^{\cdot-}$ is more facile than from $DMA^{\cdot+}$, and this leads to a higher yield of addition product.

In summary, photoinduced reactions of CH derivatives with TEA lead to extensive hydrodimerizations of CH to give products **2–6**, of which the (±) diketone **4** and the dimer **5** derived from the 1,2-anion radical of CH are unknown new products in CH reduction reactions. Photoinduced reactions of CH derivatives with DMA, on the contrary, gave a CH–DMA addition product by radical pair combination, together with the dihydrodimers. In these reactions, initial electron transfer from amines to CH derivatives followed by proton transfer gave the CH anion radical **7** and their conjugate acids **9** successively. In-cage CH ketyl–α-aminoalkyl recombination affording the addition products **16–18** competes with out-of-cage radical addition of $CH^{\cdot-}$ and CH ketyl radical to CH molecule, leading to the dihydrodimers **2–6**. Therefore different ratios of CH–DMA addition to CH hydrodimerization products are formed, depending on amine structure and reaction conditions. This product ratio A/H reflects the influences of different factors on the competition of in-cage and out-of-cage processes, which include steric hindrance of the α-aminoalkyl radicals towards addition to the C=C bond of CH, thermodynamic acidities of amine cation radicals, solvent polarities and special salt effects.

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References

[1] S.G. Cohn, A. Parola and G.H. Parsons, *Chem. Rev.*, *73* (1973) 141; P.J. Wagner, *Top. Curr. Chem.*, *66* (1976) 1; M. Hoshino and H. Shizuka, in M.A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Elsevier, New York, 1988, Part C, Chapter 4.5, pp. 313–371.

[2] R.C. Cookson, J. Hudec and N.A. Mirza, *J. Chem. Soc., Chem. Commun.*, (1968) 180.

[3] (a) N.J. Pienta and J.E. Mckimmey, *J. Am. Chem. Soc.*, *104* (1982) 5501; (b) D.W. Smith and N.J. Pienta, *Tetrahedron Lett.*, (1984) 915.

[4] (a) U.C. Yoon and P.S. Mariano, *Acc. Chem. Res.*, *25* (1992) 233; (b) D.I. Schuster, in S. Patai and Z. Rapoport (eds.), *The Chemistry of Enones*, Wiley, Chichester, West Sussex, 1989, pp. 623–756; (c) N.J. Pienta, in M.A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Elsevier, New York, 1988, Part C, Chapter 4.7, pp. 421–486.

[5] (a) D.I. Schuster and A.M. Insogna, *J. Org. Chem.*, *56* (1991) 1879; (b) Y.T. Jeon, C.P. Lee and P.S. Mariano, *J. Am. Chem. Soc.*, *113* (1991) 8847; W. Xu, X.M. Zhang and P.S. Mariano, *J. Am. Chem. Soc.*, *113* (1991) 8863; (c) R.S. Givens, R. Singh, J.Y. Xu and Y.H. Park, *Tetrahedron Lett.*, (1990) 6793; (d) J. Mattey, A. Banning, E.W. Bischof, A. Heildbreder and J. Runsink, *Chem. Ber.*, *125* (1992) 2119.

[6] (a) C. Harries and F. Hübner, *Ann.*, *296* (1897) 295; A. Russel, J. Todd and C. Wilson, *J. Chem. Soc.*, (1934) 1940; L.R. Finch and D.E. White, *J. Chem. Soc.*, (1950) 3367; (b) M. Gaweda, B. Kawalek, L. Lebioda, J. Mirek and M. Ciechanowicz-Rutkowska, *Pol. J. Chem.*, *52* (1978) 1747.

[7] (a) B. Pandey, R.K. Tikare, M. Muneer, P.V. Kamat and M.V. George, *Chem. Ber.*, *119* (1986) 917; (b) E.L. Totton, R.T. Bass, Jr., F.N. Kiruti and B. Twitty, *J. Org. Chem.*, *46* (1981) 3547.

[8] J.B. Conant and H.B. Cutter, *J. Am. Chem. Soc.*, *48* (1926) 1016.

[9] M. Morioka, Y. Takeuchi, H. Mizuno and M. Suzuki, *Nippon Kagaku Kaishi*, (1980) 1300; *Chem. Abstr.*, (1980) 94-65262.

[10] H. Stamm, A. Sommer, A. Onistschenko and A. Woderer, *J. Org. Chem.*, *51* (1986) 4979.

[11] (a) K. Takaki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku and Y. Fujiwara, *J. Chem. Soc., Chem. Commun.*, (1990) 516; K. Takaki, K. Nagase, F. Beppu and Y. Fujiwara, *Chem. Lett.*, (1991) 1665; (b) K. Takaki, F. Beppu, I. Nakagawa and Y. Fujiwara, *Chem. Lett.*, (1992) 535.

[12] A.Z. Rubezhov, *Tetrahedron Lett.*, *25* (1977) 2189.

[13] (a) R. Pasternak, *Helv. Chim. Acta*, *31* (1948) 753; I.A. Korshunov and Yu. V. Vodzinskiy, *Zh. Fiz. Khim.*, *27* (1953) 1152; P.J. Simonet and A. Albisson, *Bull. Soc. Chim. Fr.*, (1971) 1125; (b) F. Fournier, J. Berthelot and J.-J. Basselier, *Tetrahedron*, *41* (1985) 5667.

[14] A. Hinig, *Chem. Ber.*, *11* (1952) 1056.

[15] A.T. Nielson and W.J. Haulihan, *Org. Reactions*, *16* (1968) 44.

[16] (a) M. Okubo, *Bull. Chem. Soc. Jpn.*, *50* (1977) 2379. (b) J. Harboar and A.V. Guzzo, *Mol. Phys.*, *20* (1971) 565; *23* (1973) 151.

[17] (a) Z. Dinya, S. Kiss, J. Balint and R. Bognar, *Stud. Org. Chem.*, *23* (1986) 93–101. (b) V.G. Mitina, B.A. Zadorozhnyi and V.F. Lavrushin, *Zh. Obshch. Khim.*, *45* (1975) 2713; V.G. Mitina, M. Reinhardt and V.F. Lavrushin, *Zh. Obshch. Khim.*, *50* (1980) 134; M. Reinhardt, A.A. Sukhorukov, A. Raushal and V.F. Lavrushin, *Khim. Geterotsikl. Soedin.*, (1977) 1202. (c) G. Montaudo and S. Caccamese, *J. Org. Chem.*, *38* (1973) 710; S. Caccamese, J.A. McMillan and G. Montaudo, *J. Org. Chem.*, *43* (1978) 2703.

[18] S.W. Baldwin, *Org. Photochem.*, *5* (1981) 123; P.J. Wagner and D.J. Bucheck, *J. Am. Chem. Soc.*, *91* (1969) 5090.

[19] H. Miyasaka, K. Morila, M. Kiri and N. Mataga, *Ultrafast Phenomenon*, Vol. VII, Springer, Berlin, 1990, p. 498; H. Miyasaka, K. Morita, K. Kamada and N. Mataga, *Bull. Chem. Soc. Jpn.*, *63* (1990) 3385; H. Miyasaka, M. Morita, K. Kamada, K. Kiri, T. Nagata and N. Mataga, *Bull. Chem. Soc. Jpn.*, *64* (1991) 3229; H. Miyasaka, T. Nagata, M. Kiri and N. Mataga, *J. Phys. Chem.*, *96* (1992) 8060.

[20] K.S. Peters and J. Lee, *J. Phys. Chem.*, *97* (1993) 3761.

[21] D.I. Schuster, I.M. Nunez and C.B. Chan, *Tetrahedron Lett.*, (1981) 1187.

[22] R. Bonneau, *J. Am. Chem. Soc.*, *102* (1980) 3816; D.I. Schuster, R. Bonneau, D.A. Dunn, J.M. Rao and J. Joussot-Dubien, *J. Am. Chem. Soc.*, *106* (1984) 2706; D.A. Dunn, D.I. Schuster and R. Bonneau, *J. Am. Chem. Soc.*, *107* (1985) 2802; D. Weir, J.C. Scaiano and D.I. Schuster, *Can. J. Chem.*, *66* (1988) 2595; D.I. Schuster, G.E. Heibel, P.B. Brown, N.J. Turro and C.V. Kumar, *J. Am. Chem. Soc.*, *110* (1988) 8261; D.I. Schuster, D.A. Dunn, G.E. Heibel, P.B. Brown, J.M. Rao, J. Woning and R. Bonneau, *J. Am. Chem. Soc.*, *113* (1991) 6245.

[23] R.A. Caldwell and M. Singh, *J. Am. Chem. Soc.*, *105* (1983) 5139.

[24] A. Weller, *Z. Phys. Chem. (Wiesbaden)*, *133* (1982) 93.

[25] B.H. Lipshutz, R.S. Wilhelm, S.T. Nugent, R.D. Little and M.M. Baizer, *J. Org. Chem.*, *48* (1983) 3306.
[26] (a) K.S. Peters, S.C. Freilich and C.G. Shaeffer, *J. Am. Chem. Soc.*, *102* (1980) 5701; C.G. Sheafer and K.S. Peters, *J. Am. Chem. Soc.*, *102* (1980) 7567; J.S. Simon and K.S. Peters, *J. Am. Chem. Soc.*, *103* (1981) 6403; L.E. Manring and K.S. Peters, *J. Am. Chem. Soc.*, *107* (1985) 6452; (b) J. D. Simon and K.S. Peters, *J. Am. Chem., Soc.*, *106* (1984) 6452; J.D. Simon and K.S. Peters, *J. Am. Chem. Soc.*, *105* (1983) 4875.
[27] E. Haselbach, E. Vauthey and P. Suppan, *Tetrahedron*, *44* (1988) 7335.
[28] A. Demeter, L. Biczok, T. Berces, V. Wintgens, P. Valat and J. Kossanyi, *J. Phys. Chem.*, *97* (1993) 3217.
[29] E. Hayon, J. Ibata, N.N. Lichtin and M. Simic, *J. Phys. Chem.*, *76* (1972) 2072; J. Lilie and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, *73* (1969) 170.
[30] S. Das and C. von Sonntag, *Z. Naturforsch.*, *41b* (1986) 505.
[31] D. Griller and D.D.M. Wayner, *Pure Appl. Chem.*, (1989) 717.
[32] T. Hino, H. Hakazawa, H. Masuhara and N. Mataga, *J. Phys. Chem.*, *80* (1976) 33.
[33] K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann. Chem.*, *1* (1963) 661.
[34] M.J. Kamlet, J.-L.M. Abboud, M.H. Abraham and R.W. Taft, *J. Org. Chem.*, *48* (1983) 2877.
[35] S. Winstein and G.C. Robinson, *J. Am. Chem. Soc.*, *80* (1958) 269.
[36] K. Mizuno, N. Ichnose and Y. Otsuji, *Chem. Lett.*, (1985) 455; T. Tame, K. Mizuno, I. Hashita and Y. Otsuji, *J. Org. Chem.*, *57* (1992) 5338; K. Gollnick, X.L. Xiao and V. Paulmann, *J. Org. Chem.*, *55* (1990) 5945.
[37] E. Hasegawa, W. Xu, P.S. Mariano, U.C. Yoon and J.U. Kim, *J. Am. Chem. Soc.*, *110* (1988) 8099.
[38] V.D. Parker and M. Tilset, *J. Am. Chem. Soc.*, *113* (1991) 8778.
[39] X.M. Zhang, S.R. Yeh, S. Hong, M. Freccero, A. Albini, D.E. Falvey and P.S. Mariano, *J. Am. Chem. Soc.*, *116* (1994) 4211