Photo Diels-Alder Additions, IV[1]

1,4-Photoaddition of α-(*tert*-Butylthio)acrylonitrile to Acylnaphthalenes

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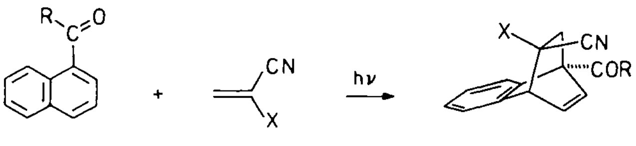
Photoexcited 1-naphthaldehyde (1a), 1-acetonaphthone (1b) and 2-naphthaldehyde (4) add α-(*tert*-butylthio)acrylonitrile (2b) in a [4 + 2] mode with highly regio- and stereoselective formation of only one diastereomer of one of the two possible regioisomeric 1,4-dihydro-1,4-ethanonaphthalenes. The configuration of the products is unambiguously derived from an X-ray crystal structure analysis for adduct 3e and an NOE experiment for compound 5. The only adduct from 1a and 2b could be detected spectroscopically but decomposed upon attempted chromatographic separation of the photolysate. Adducts 3e and 5 show first-order retro-cleavage into the starting materials at 50°C in CDCl$_3$ solution with half-lifes of 4.8 d and 11 h, respectively.

Photo-Diels-Alder-Additionen, IV[1]. — 1,4-Photoaddition von α-(*tert*-Butylthio)acrylonitril an Acylnaphthaline

1-Naphthaldehyd (1a), 1-Acetonaphthon (1b) und 2-Naphthaldehyd (4) addieren bei elektronischer Anregung α-(*tert*-Butylthio)-acrylonitril nach einem [4 + 2]-Modus unter hoch regio- und stereoselektiver Bildung eines einzigen Diastereomers von nur einem der beiden möglichen regioisomeren 1,4-Dihydro-1,4-ethanonaphthaline. Die Konfiguration der Produkte konnte eindeutig durch eine Röntgenstrukturanalyse (im Fall des Adduktes 3e) sowie ein NOE-Experiment (im Falle der Verbindung 5) geklärt werden. Das einzige Addukt aus 1a und 2b konnte spektroskopisch detektiert werden, es zerfiel jedoch beim Versuch der chromatographischen Auftrennung des Photolysats. 3e und 5 zerfallen nach 1. Ordnung bei 50°C in CDCl$_3$-Lösung mit Halbwertszeiten von 4.8 d bzw. 11 h in die Ausgangsmaterialien.

α-Morpholinoacrylonitrile (**2a**) in various solvents undergoes a highly regio- and stereoselective 1,4-addition to the skeleton of 1-acylnaphthalenes **1a – c** with formation of 1-acyl-9-morpholino-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitriles **3a – c** as the practically sole products[2]. Light-induced additions of alkenes to the naphthalene skeleton had — with but one exception[3] — hitherto been unknown for acylnaphthalenes, but are well-known for naphthalene itself[4], 1- and 2-naphthonitrile[5] and 2-naphthyl methyl ether[6]. Generally, [2 + 2] additions are observed[4–6], but [4 + 2] additions also occur[3,4].



1a-c

a : R = H
b : R = Me
c : R = Ph

2a,b

a : X = morpholino
b : X = S-tBu

3a-e

a : R = H, X = morpholino
b : R = Me, X = morpholino
c : R = Ph, X = morpholino
d : R = H, X = S-tBu
e : R = Me, X = S-tBu

Whereas the direction of addition of **2a** as well as of other aminoacrylonitriles[7] could be easily delineated from the conventional ^{1}H NMR spectra of the products **3a – c**, the stereochemistry at C-9 and other structural details of **3b** have been determined by an X-ray crystal structure analysis[2]. The *endo* orientation of the morpholino group as present in **3b** has also been assumed to be the likely orientation in **3a,c** by comparison of the relevant chemical shifts in **3a – c**[1a].

The remarkable regio- and stereoselectivity observed so far as well as the efficient asymmetric induction in the photo Diels-Alder addition of both enantiomers of α-(2-methoxymethyl)-1-pyrrolidinylacrylonitrile to **1b** (the enantiomeric excesses of the products exceed 96%)[8] still await a conclusive explanation.

We wish to report further examples of this photoaddition which show the same regio- and stereoselectivities, i.e., the products show solely *endo* orientation of the C-9 donor group.

From comparison of the UV spectra (taken in cyclohexane solution) of **1a** and **1b** with that of **2b**, it may be concluded that more than 95% of the 313-nm emission and practically all of the 366-nm emission of the high-pressure mercury burner will be absorbed by **1a** and **1b**, respectively, when equimolar solutions are used.

Irradiation (λ ⩾ 280 nm) of 0.1 M solutions of **1a** or **1b**, respectively, in benzene containing equimolar amounts of α-(*tert*-butylthio)acrylonitrile[9] (**2b**) under nitrogen resulted in formation of C=O deconjugated products. This was monitored for the conversion of **1a** by a new IR absorption at ν = 1725 cm^{-1} (representing **3d**) at the expense of the 1690-cm^{-1} band of **1a**, and for the formation of **3e** by a new band at ν = 1710 cm^{-1} at the expense of the 1675-cm^{-1} C=O absorption of starting material **1b**.

All attempts to isolate **3d**, however, failed due to its instability towards chromatography on silica gel, but the ^1H NMR spectrum of the crude reaction mixture did show characteristic resonances assignable to a 1:1 1,4-adduct of **2b** to **1a** (see experimental part).

The 1:1 adduct of **2b** to **1b**, however, could be isolated by preparative layer chromatography, and aside from its ^1H and ^{13}C NMR spectral characterization, its structure was unambiguously demonstrated by an X-ray crystal structure analysis[10] (see Figure 1 and Tables 1,2).

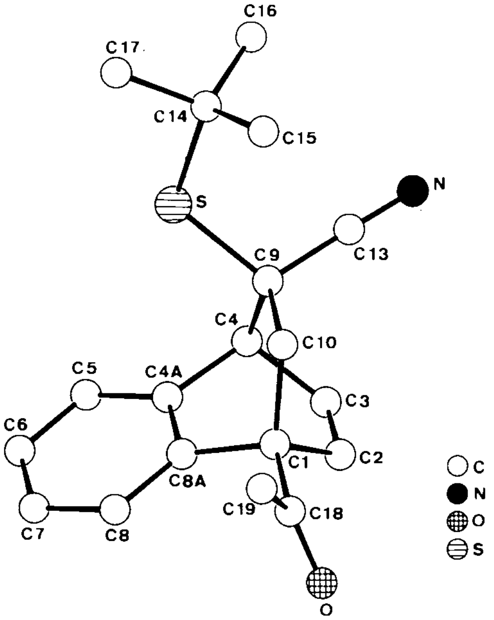


Figure 1. Molecular structure of rel-(1*R*,4*R*,9*R*)-1-acetyl-9-(*tert*-butylthio)-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitrile (**3e**) in the crystal

Table 1. Selected interatomic distances [Å] and angles [°] of **3e**

(a) Distances

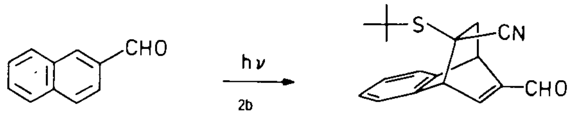
C1 - C2	1.526(3)	C4 - C4a	1.511(3)
C1 - C8a	1.533(3)	C4 - C9	1.587(3)
C1 - C10	1.569(3)	C4a - C8a	1.397(3)
C2 - C3	1.314(4)	C9 - C10	1.573(3)
C3 - C4	1.514(3)	C9 - C13	1.479(3)

(b) Angles

C1 - C2 - C3	114.7(2)	C9 - C4 - C4a	106.3(2)
C2 - C3 - C4	114.9(2)	C4 - C9 - C13	107.7(2)
C3 - C4 - C4a	108.5(2)	C13 - C9 - S	110.0(1)
C4 - C4a - C8a	113.5(2)	C10 - C9 - S	114.2(1)
C4a - C8a - C1	112.7(2)	C4 - C9 - S	105.8(1)
C8a - C1 - C2	107.4(2)	C13 - C9 - C10	110.6(2)
C8a - C1 - C10	105.6(2)	C18 - C1 - C10	113.3(2)
C2 - C1 - C10	106.2(2)	C18 - C1 - C2	112.9(2)
C1 - C10 - C9	109.3(2)	C18 - C1 - C8a	111.1(2)
C10 - C9 - C4	108.2(2)	C9 - S - C14	109.7(1)
C9 - C4 - C3	105.2(2)		

The bonds C1–C10, C4–C9, and C9–C10 are slightly elongated, and a similar trend has been observed for the adduct **3b**[2]. These bond elongations and angular distortions are indicative of ring strain, and are in line with the observed tendency for thermal retro-cleavage into the starting materials (see below).

While no chemical reaction could be observed between photoexcited 1-naphthophenone (**1c**) or photoexcited 2-acetonaphthone and **2b**, the latter was added to 2-naphthaldehyde (**4**) with formation of again one single 1,4-adduct **5** in moderate yield (27%). While at the beginning of the experiment 90% of the 313-nm and virtually all of the 366-nm emission of the lamp used can be expected to be absorbed by **4**, the product **5** with its broad shoulder at 340 nm and its absorption tail towards 380 nm is likely to act as a screen as the photoaddition proceeds. Thus, a better yield may not be expected.



4 5

The structure of **5** is unambiguously derived from the analysis of its 300-MHz ^1H NMR spectrum (including decoupling experiments on the basis of the 80-MHz ^1H NMR spectrum using C_6D_6 as solvent). The doublet (J = 6.2 Hz) at δ = 4.09 ppm for one proton is assigned to 4-H, since it shows coupling only to one proton (3-H, δ = 6.56 ppm). 10-H_2 and 1-H form an ABX system, the X part of which shows additional coupling to 3-H, since irradiation into the 1-H signal (at δ = 4.44 ppm) simplifies both the AB portion of the ABX system and the signal of 3-H. Irradiation into the center of the 3-H signal turns the 4-H doublet into a singlet and simplifies the 1-H multiplet.

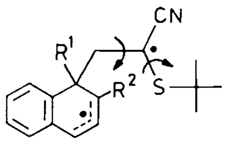
The *syn* orientation of the *tert*-butylthio group and the benzenoid ring has been corroborated by a nuclear Overhauser effect signal intensity difference determination. Irradiation at the resonance frequency of the *tert*-butyl protons leads to an intensity enhancement for the lowest field portion of the 4H aryl multiplet, and this clearly establishes the spatial neighbourhood between aromatic ring and the *tert*-butylthio moiety. The 3-H and formyl signals are not affected.

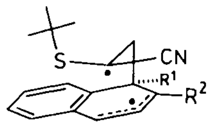
Another property of adducts **3e** and **5** which may affect yields is their limited thermal stability. First-order decays have been found in both cases when the retro-cleavage was followed in $CDCl_3$ solution (original concentration 0.1 M) at (50 ± 0.5)°C NMR spectroscopically. The following decay rate constants and half lifes have been determined. **3e**: $1.6 \times 10^{-6}\,s^{-1}$, $\tau_{1/2}$ = 4.8d; **5**: $1.7 \times 10^{-5}\,s^{-1}$, $\tau_{1/2}$ = 11 h.

Photophysical and other details of these additions will be treated in a forthcoming publication. On the basis of the evidence available so far[1a,b,2,8] it may be tentatively concluded that

– the triplet excited naphthalenes **1a**, **b**, and **4** add **2b** regioselectively to form 1,4-diradicals as **6** and **7**, which are captodatively[11] stabilized on one end and have considerable delocalization at the other terminus,

– the observed stereoselectivity is brought about by secondary electrostatic effects in the available product-like conformations **6P** or **7P**, respectively; that these added electrostatic effects stabilize these conformations and direct them preferentially to the products,





6 R^1 = CHO or $COCH_3$, R^2 = H 6P
7 R^1 = H, R^2 = CHO 7P

– other conformations than **6P**, **7P**, which do not experience that extra stabilization, revert to starting materials, and

– other constitutionally isomeric 1,4-diradicals are either not formed or solely revert to starting materials in preference to ring closure.

Clearly, more investigations are needed before more rigorous conclusions may be drawn.

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Experimental

All melting points have been determined with a Kofler microscope (Reichert Thermovar) and are uncorrected – ^{1}H NMR spectra: Varian EM 360 (60 MHz) or Bruker WP 80 (80 MHz) and WM 300 (300 MHz). – ^{13}C NMR spectra: Bruker WM 300 (75.5 MHz). – IR spectra: Perkin-Elmer 397. Mass spectra (70 eV, EI mode, temperature of inlet system given): MAT 311 A spectrometer. Elemental analyses: Carlo Erba 1106 CHN analyzer (Duisburg) and Mikroanalytisches Labor Pascher, Bonn. – Solvents used were purified by general methods prior to use. – Preparative layer chromatography (PLC) has been carried out on 48-cm wide and 20-cm high plates covered with a slurry-applied and air-dried 1-mm layer of Merck silica gel PF_{254}. – All irradiations have been carried out using a 150-W high-pressure Hg vapour lamp through a water-cooled immersion well made of Duran glass ($\lambda \geqslant$ 280 nm). – UV spectra: Perkin-Elmer 554 (sh = shoulder).

Irradiation of 1-Naphthaldehyde (**1a**) *in the Presence of α-(tert-Butylthio)acrylonitrile* (**2b**): A solution of 1.952 g (12.5 mmol) of **1a** and 1.765 g (12.5 mmol) of **2b** in 125 ml of dry benzene was irradiated for 120 h, during which period the solution assumed a faint red colour. After concentration at room temperature, the IR (film between plates) of the residue showed an additional absorption at 1725 cm^{-1} (C=O of adduct **3d**). – 80-MHz ^{1}H NMR ($CDCl_3$): Besides signals assigned unambiguously to the starting materials used, the following were detected and attributed to compound **3d**: AB (δ_A = 2.15, δ_B = 2.58, $|{}^2J_{AB}|$ = 12.8 Hz, 10-H_2, δ = 10.36 (s, 1 H, CHO). Other resonances could not be assigned unambiguously. – Attempted separation by PLC resulted in the recovery of starting materials only.

rel-(1R,4R,9R)-1-Acetyl-9-(tert-butylthio)-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitrile (**3e**): A solution of 2.128 g (12.5 mmol) of **1b** and 1.765 g (12.5 mmol) of **2b** in 125 ml of cyclohexane was irradiated for 96 h and concentrated. PLC (pentane/ether, 3:1) gave zone 1 (R_f = 0.47), 115 mg of **2b**; zone 2 (R_f = 0.34) 847 mg (40% recovery) of **1b**; zone 3 (R_f = 0.2), 1.970 g (51% based on not recovered **1b**) of cycloadduct **3e**, m.p. 106–108°C (from hexane), zone 4 (R_f = 0.14) 130 mg of unidentified polar material. – IR (KBr): ν = 2230 cm^{-1} (CN), 1715 (CO). – 300-MHz ^{1}H NMR (C_6D_6): δ = 1.28 (s, 9H, tBu), 1.89 (s, 3H, $COCH_3$), AB (δ_A = 2.28, δ_B = 2.46, $|{}^2J_{AB}|$ = 13.1 Hz, 10-H), ABX [δ_X = 4.03 (${}^3J_{AX}$ + ${}^4J_{BX}$ = 7.3 Hz), 4-H; δ_A = 6.44, 3-H; δ_B = 6.39, 2-H; ${}^3J_{AB}$ = 7.8 Hz, ${}^3J_{AX}$ = 6.2 Hz, ${}^4J_{BX}$ = 1.2 Hz], 6.70–7.05 (m, 4H, aromatic H). – 75.47-MHz ^{13}C NMR ($CDCl_3$): δ = 28.82 (q, *J* = 128 Hz, $CO\mathit{C}H_3$); 32.01 [q, *J* = 127.2 Hz, additionally split by coupling with protons of the neighbouring methyl groups, $C(\mathit{C}H_3)_3$]; 42.79 (s); 46.71 (t, *J* = 139.8 Hz, C-10); 48.17 (s, C-9); 50.26 (d, *J* = 146.1 Hz, C-4), 59.40 (s, C-1); C-5, -6, -7, -8 at 120.85 (d, *J* = 157.7 Hz), 126.13 (d, *J* = 161 Hz), 126.91 (d, *J* = 160.4 Hz), 126.97 (d, *J* = 162.6 Hz); 122.87 (s, CN); C-4a and -8a at 137.35 (s) and 141.13 (s); 206.87 (s, CO). – UV ($CHCl_3$): λ (lg ε) = 290 nm, sh (1.38), 266 sh (2.238), 260 sh (2.372). – MS (91°C): *m/z* (%) = 311 (1.5, M^+), 269 (11), 213 (14), 212 (9), 180 (23), 170 (68), 155 (100), 141 (15), 127 (56), 57 (86).

$C_{19}H_{21}NOS$ (311.4)					
	Calcd.	C 73.27	H 6.79	N 4.50	S 10.29
	Found	C 73.19	H 6.80	N 4.56	S 10.3

X-ray Structural Analysis of **3e**: Crystal size 0.29 × 0.36 × 0.54 mm, colourless; *a* = 1227.9(1) pm, *b* = 1393.8(2) pm, *c* = 1003.7(1) pm, β = 99.55(1)°; *V* = 1694 · 10^6 pm^3, d_{calcd} = 1.22 gcm^{-3}, *Z* = 4, space group $P2_1/c$ (no. 14); μ = 1.83 cm^{-1}, λ = 71.069 pm; Nonius CAD-4 diffractometer; unique reflections 3800, observed reflections 2793 [$I > 2\,\sigma(I)$], refined parameters 199; *R* = 0.044, R_w = 0.053 [$w = 1/\sigma^2(F_o)$]$^{10)}$.

Attempted Addition of **2b** *to* **1c**: A solution of 2.903 g (12.5 mmol) of 1-naphthophenone (**1c**) and 1.765 g (12.5 mmol) of **1b** was irradiated for 90 h, during which time no new carbonyl absorption developed in the IR spectrum as evidenced from samples withdrawn periodically. The ^{1}H NMR spectrum of the solution did not reveal any other signals than those unambiguously assigned to the starting materials.

Table 2. Atomic coordinates and averaged thermal parameters [Å^2] for **3e**

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij}\, a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$$

Atom	x	y	z	U_{eq}
S	0.3196(1)	0.0692(1)	0.1082(1)	0.044
O	0.0453(2)	-0.3056(1)	-0.0493(2)	0.087
N	0.4922(2)	-0.1276(2)	0.2733(2)	0.057
C1	0.1692(2)	-0.1752(1)	-0.0044(2)	0.038
C2	0.2632(2)	-0.2411(2)	-0.0284(2)	0.051
C3	0.3530(2)	-0.1966(2)	-0.0494(2)	0.051
C4	0.3468(2)	-0.0882(2)	-0.0460(2)	0.040
C4A	0.2452(2)	-0.0565(1)	-0.1422(2)	0.036
C5	0.2423(2)	0.0128(2)	-0.2417(2)	0.043
C6	0.1424(2)	0.0336(2)	-0.3234(2)	0.049
C7	0.0473(2)	-0.0142(2)	-0.3058(2)	0.050
C8	0.0497(2)	-0.0828(2)	-0.2046(2)	0.045
C8A	0.1490(2)	-0.1039(1)	-0.1222(2)	0.036
C9	0.3249(2)	-0.0626(1)	0.1013(2)	0.035
C10	0.2151(2)	-0.1138(1)	0.1236(2)	0.037
C13	0.4196(2)	-0.0986(2)	0.1988(2)	0.041
C14	0.3449(2)	0.1096(2)	0.2873(2)	0.049
C15	0.2867(2)	0.0472(2)	0.3776(3)	0.070
C16	0.4677(2)	0.1154(2)	0.3411(3)	0.061
C17	0.2946(2)	0.2101(2)	0.2757(3)	0.079
C18	0.0635(2)	-0.2299(2)	0.0089(2)	0.053
C19	-0.0166(2)	-0.1869(2)	0.0873(3)	0.069

Attempted Addition of **2b** *to 2-Acetonaphthone:* A solution of 1.702 g (10 mmol) of 2-acetonaphthone and 1.412 g (10 mmol) of **2b** in 100 ml of cyclohexane was irradiated for 21 h. The residue obtained on concentration contained only the starting materials, as evidenced from the IR and ^{1}H NMR spectra.

rel-(1R,4R,9R)-9-(tert-Butylthio)-2-formyl-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitrile (**5**): A solution of 1.952 g (12.5 mmol) of 2-naphthaldehyde (**4**) and 1.765 g (12.5 mmol) of **2b** in 125 ml of cyclohexane was irradiated for 70 h and concentrated. PLC (pentane/ether, 2:1) gave zone 1 (R_f = 0.56), containing only unreacted **2b**; zone 2 (R_f = 0.38), 1.225 g (63% recovery) of **4**; zone 3 (R_f = 0.27), 370 mg (27%, based on not recovered **4**) of crystals, m.p. 98–101°C (from hexane); zone 4 (R_f = 0.2), containing 222 mg of a mixture of four compounds). – IR (KBr): $\nu = 2230\ \mathrm{cm}^{-1}$ (CN), 1675 (conjugated CO). – 300-MHz ^{1}H NMR ($CDCl_3$): δ = 1.48 (s, 9H, tBu), ABX ($\delta_A = 2.52$, $\delta_B = 1.92$, $\delta_X = 4.61$, $|^2J_{AB}| = 13.1$, $^3J_{AX} = 3.1$, $^3J_{BX} = 2.3$ Hz, 10-$H_{A,B}$, 1-H_X), 4.63 (m, 1H, 4-H), 7.17–7.32 (m, 4H, aromatic H, 7.56 (dd, $^3J_{3,4} = 6.2$, $^4J_{3,1} = 1.7$ Hz, 1H, 3-H), 9.61 (s, 1H, CHO). – (C_6D_6): δ = 1.23 (s, 9H, *t*Bu), ABX ($\delta_A = 2.08$, $\delta_B = 1.61$, $\delta_X = 4.43$, $|^2J_{AB}| = 13.1$, $^3J_{AX} = 3.1$, $^3J_{BX}$ = 2.3 Hz, 10-$H_{A,B}$, 1-H_X), 4.09 (d, $^3J_{4,3} = 6.2$ Hz, 1H, 4-H), 6.64 (dd, $^3J_{3,4} = 6.2$, $^4J_{1,3} = 1.7$ Hz, 1H, 3-H), 6.83–7.00 (m, 4H, aromatic H), 9.14 (s, 1H, CHO). – 75.47-MHz ^{13}C NMR ($CDCl_3$): δ = 31.83 [q, J = 127.4 Hz, C(CH$_3$)$_3$], 36.11 (d, J = 144.6 Hz, C-1), 41.46 [s, C(CH$_3$)$_3$], 44.56 (t, J = 139.2 Hz, C-10), 48.39 (s, C-9), 50.49 (d, J = 147.4 Hz, C-4), 122.61 (s, CN), signals at 123.57 (d, J = 151.1 Hz), 126.10 (d, J = 162.9 Hz), 126.80 (d, J = 157.5 Hz) and 127.59 (d, J = 160.8 Hz) for C-5, -6, -7 and -8; s at 135.72 and 140.49 for C-4a and -8a; 150.01 (d, $^2J_{C,H(CHO)} = 26.5$ Hz, C-2), 151.52 (d, J = 172.4 Hz, C-3), 187.77 (d, J = 177.7 Hz, CHO). – UV ($CHCl_3$): λ[nm] (lg ε) = 344 nm, sh (1.360) 326 sh (1.461), 260 sh (3.211) 250 sh (3.278). – EI-MS (70 eV, 114°C): m/z (%) = 156 (100), 141 (15), 127 (51), 101 (5). – (18 eV, 114°C): m/z (%) = 156 (100), 141 (17). – FD-MS (–4.5 kV, 0 mA): m/z (%) = 297 (38, M^+), 156 (100), 141 (62), 84 (28).

$C_{18}H_{19}NOS$ (297.4) Calcd. C 72.69 H 6.44 N 4.71 S 10.78
Found C 72.60 H 6.46 N 4.71 S 10.7

Thermal Cleavage of **3e** *and* **5**: In a sealed NMR tube a 21-mg sample of **3e** in 0.7 ml of $CDCl_3$ was kept at (50 ± 0.5)°C and the 80-MHz ^{1}H NMR spectrum was recorded initially, after 24 h, and thereafter in 48 h intervals. After 15 days, 88% of **3e** had been cleaved into starting materials **1b** and **2b**, which were clearly identified by their signals in the mixture. A first half life of 4.8 d could be derived. Likewise, an 18.5-mg sample of **5** was kept under the same conditions, but the spectra were recorded in 2 h and 3 h intervals. After 45 h, a 91% cleavage into **4** and **1b** was evident. A half life of 11 h could be derived for **5**.

CAS-Registry-Nummern

1a: 66-77-3 / **1b**: 941-98-0 / **1c**: 642-29-5 / **2b**: 72314-64-8 / **3d**: 118043-05-3 / **3e**: 118139-69-8 / **4**: 66-99-9 / **5**: 118043-06-4 / 2-acetonaphthone: 93-08-3

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