

Photocycloadditions of four homologous 2-(cycloamino)-propenenitriles to 1-acetonaphthone

Dietrich Döpp,* Claudia Kruse, Ayman W. Erian, and Michael Pies

Institut für Organische Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

E-mail: dietrich.doepp@uni-due.de

Abstract

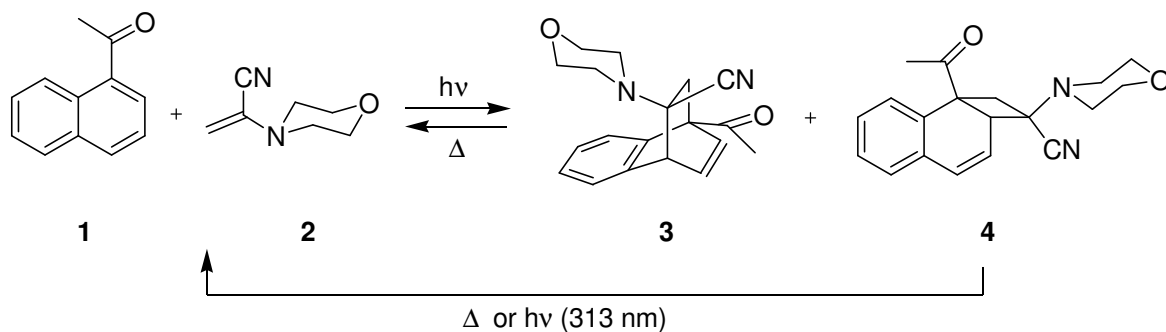
2-(Cycloamino)propenenitriles $\text{H}_2\text{C}=\text{C}(\text{CN})\text{N}(\text{CH}_2)_n$ ($n = 4, 5, 6, 7$) are added to triplet π,π^* -excited 1-acetonaphthone forming 8b-acetyl-2-(cycloamino)-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-2-carbonitriles as well as 1-acetyl-9-(cycloamino)-1,4-dihydro-1,4-ethanonaphthalene-9-carbonitriles. Regio- and stereoselectivity of the photocycloadditions and the special role of the cyclobuta[*a*]naphthalene adducts in the initial stage of the photoadditions are discussed.

Keywords: 1-Acylnaphthalenes, α -cyanoenamines, light-sensitive photocycloadducts, π,π^* triplet reactivity, selectivity phenomena

Introduction

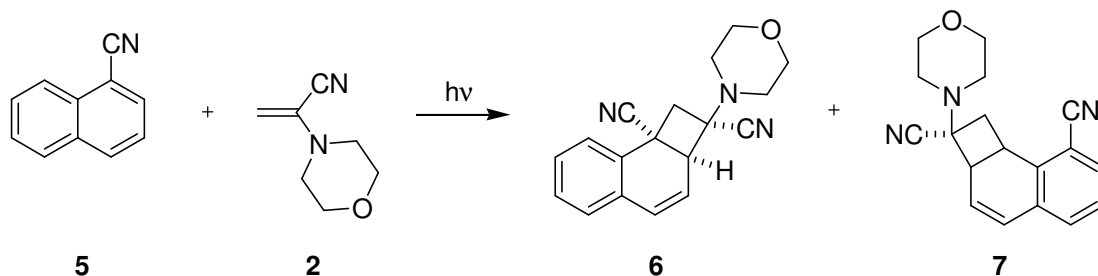
So-called captodatively substituted¹⁻³ alkenes, especially 2-aminopropenenitriles such as **2**, undergo a variety of photocycloadditions to fused arenes.⁴ 2-Morpholinopropenenitrile (**2**)⁵ had been used preferentially in our earlier studies for its crystallinity and easy purification by crystallization, and for its easy removal from reaction mixture residues by vacuum sublimation.

It had earlier been demonstrated that **2** may readily undergo a [4+2]-cycloaddition to photoexcited 1-acetonaphthone (= 1-(1-naphthyl)ethanone, **1**) – a prototypical 1-acylnaphthalene – giving rise to *rel*-(1*R*,4*R*,9*R*)-1-acetyl-1,4-dihydro-9-morpholino-1,4-ethanonaphthalene-9-carbonitrile (**3**).^{6,7} This reaction was later shown to proceed via a low-lying excited triplet state of **1**.^{8,9} There also was indication for the formation of a minor [2+2]-adduct, namely 8b-acetyl-1,2,2a,8b-tetrahydro-2-morpholinocyclobuta[*a*]naphthalene-2-carbonitrile (**4**)⁷ (Scheme 1). The latter compound had been found sensitive to thermal and light-induced (313 nm) reversal to the starting materials.⁷ The very low yield of **4** is in contrast to various other inter- and intramolecular [2+2]-photocycloadditions to naphthalenes, especially naphthonitriles,^{10,11} while 1,4-photocycloadditions are rare for these compounds.



Scheme 1

Our previous finding that 1-naphthonitrile (**5**), when excited in the presence of **2**, does not give rise to any 1,4-adduct, instead the two cyclobutanaphthalenes **6** and **7** were formed,¹² is in analogy to related cases in the literature^{10,11} (Scheme 2).

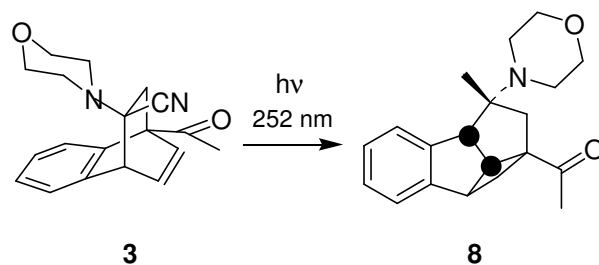


Scheme 2

While only a negligible yield of the 1,2-[2+2]-adduct **4** has been obtained from **1** and **2**, the corresponding 8-aza-analogue of **1** upon excitation in presence of **2** gave rise to a 12% yield of the analogous 1,2-adduct in addition to 32% of the analogous 1,4-[4+2]-cycloadduct,¹³ thus the 1,2 : 1,4 ratio comes close to 1:2.5. Methyl 1-naphthoate does show a reactivity analogous to that of **1** with **2** and various other α -cyanoenamines.⁴

Mode switching to practically exclusive 1,2-[2+2]-photocycloaddition of **2** and the analogous 2-(1-piperidinyl)propenenitrile (**9b**, see below) is observed for 4-R-substituted (R = OCH₃, CH₃, F, CN) acetonephthones, whereas this mode is suppressed with 2-R-substituted (R = OCH₃, CH₃) acetonephthones.¹⁴⁻¹⁶

In contrast to the rich meta-photocycloaddition chemistry of benzene,^{10,11,17,18} only a few examples of intermolecular¹⁹⁻²¹ and intramolecular^{22,23} [3+2]-photocycloadditions of alkenes to the naphthalene skeleton have been reported in the literature. Any direct [3+2]-photocycloadditions of **1** (or of any 1-acyl analogues to that) to α -cyanoenamines have not been observed by us. However, when the 1,4-adduct **3** was irradiated with 254 nm light, a formal [3+2]-photoadduct **8** was obtained⁷ (Scheme 3) via a di- π -methane rearrangement.²⁴



Scheme 3

Close inspection of the connectivity of **8** reveals that this compound could never have been formed via a direct [3+2]-photocycloaddition of **2** to **1**, but it can well be taken as the formal [3+2]-photocycloadduct of **2** to 2-acetonaphthone!

The 1,8-mode of [3+2]-photocycloaddition of alkenes to the naphthalene ring, as reported for naphthalene-1,4-dicarboxylic acid diesters,^{25,26} has not been observed so far for α -cyanoenamines and related captodative alkenes. From all of this, it has been demonstrated that photocycloadditions of captodative alkenes, especially α -cyanoenamines, to 1-acyl-naphthalenes (acyl = CHO, COCH₃, CPh, COOCH₃) and analogues thereof are governed by the following selectivities:

1. Site selectivity: Only the acyl bearing ring is affected. Also, the acyl carbonyl groups of the 1-acylnaphthalenes have never been involved in Paterno-Büchi reactions²⁷ with α -cyanoenamines.
2. Mode selectivity: Only the 1,2-[2+2]- and the 1,4-[4+2]-photocycloaddition modes but no 1,3-[3+2]-photoadditions have been observed so far.
3. Addition direction selectivity (“regioselectivity”): The head (acylnaphthalene) to tail (alkene) mode has been followed in all [2+2] and [4+2] cases.
4. Stereoselectivity: The donor group (predominantly a cyclic amino group) is preferentially oriented *syn* to the unaffected benzenoid ring in the 1,4-photocycloadducts, while the relative orientation (donor-*syn* or donor-*anti*, respectively, to the unaffected benzenoid ring) in the 1,2-photocycloadducts is less pronounced. In either case three new stereocenters are generated, and for obvious reasons, a pair of diastereomers (the C-9-epimers in the 1,4-[4+2]-addition and the C-2-epimers in the 1,2-[2+2]-addition) are to be expected as products.
5. Diastereoselectivity: Has been demonstrated earlier for the [4+2]-photocycloaddition of **1** to two chirally labeled 2-aminopropenenitriles.^{4,28}

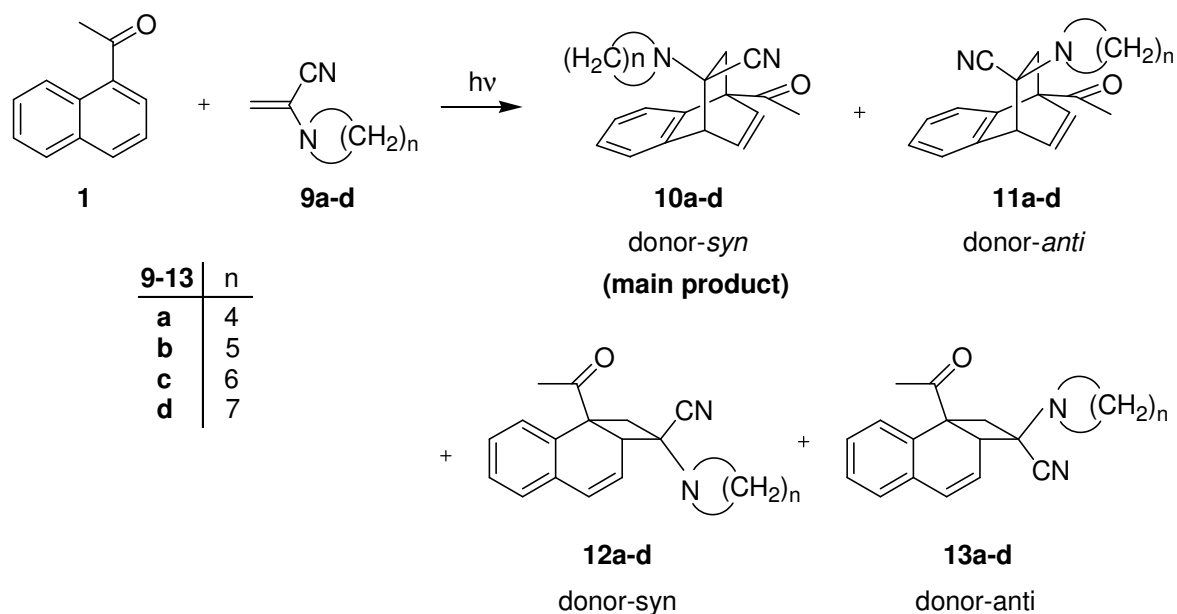
It was felt that the extension of the model photocycloaddition of **2** to **1** to a series of closely related α -cyanoenamines **9a-d** with similar electronic properties but gradually different steric requirements could cast some light on the mode, regio-, and stereoselectivities of these photocycloadditions. Thus, alkenes **9a-d**, the cyclic amino substituent of which (1-pyrrolidinyl, 1-piperidinyl, hexahydro-1*H*-azepin-1-yl, and octahydro-1-azocinyl) is in the following frequently called the “donor”, were chosen for addition to photoexcited **1**.

The energy of the lowest excited (π,π^*) triplet state of **1** has been reported to be $E_T = 236 \text{ kJ mol}^{-1}$,²⁹ its lifetime at room temperature in benzene solution is reported to be $\tau = 2 \times 10^{-4} \text{ s}$.³⁰ Nanosecond laser flash photolysis experiments⁸ had revealed that tetramethyldiazetidine 1,2-dioxide (TMDD, $E_T = 146 \text{ kJ mol}^{-1}$ ^{31,32}) quenches the T-T absorption (480 nm) of triplet **1** with $k_q = 52.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Alkenes **2**, **9a,b,c**, do quench triplet excited **1**, the rate constants being below the diffusion controlled limit, $10^{-8} \times k_q / \text{M}^{-1} \text{ s}^{-1} = 3.5 \pm 0.2$ for **2**, 28.3 ± 0.3 for **9a**, 9.0 ± 0.1 for **9b**, and 25.0 ± 0.2 for **9c** in methanol⁸. Thus, in irradiated solutions containing **1**, **2** (or **9a**) and TMDD, the latter successfully competes with the alkene in quenching triplet excited **1**.

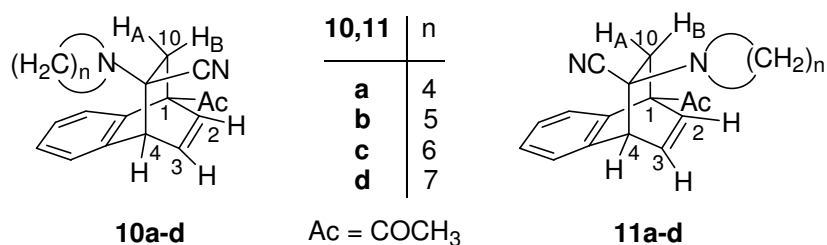
Results and Discussion

Preparative scale photocycloadditions

Preparative scale photolysis ($\lambda > 280 \text{ nm}$), run to 42-45% conversion of **1**, led to yields of 60-85% (referred to converted **1**, after refining by crystallization) of 1,4-adducts **10a-d** (Scheme 4).



Scheme 4

Table 1. Structurally relevant 300.1 MHz ^1H NMR data of products **10** and **11** (δ in ppm, J in Hz).

Entry	Solvent	Comp.	10-H _A	10-H _B	$ ^2J_{AB} $	2-H	3-H	4-H	$^3J_{2,3}$	$^4J_{2,4}$	$^3J_{3,4}$
1	CDCl ₃	10a	2.19	2.03	12.6	6.89	6.76	4.31	7.8	0.7	6.3
2	CDCl ₃	10b	2.22	1.91	12.5	6.91	6.74	4.50	7.7	0.5	6.5
3	CDCl ₃	10c	2.26	1.92	12.5	6.89	6.71	4.47	7.7	0.5	6.5
4	CDCl ₃	10d	2.19	2.13	12.7	6.91	6.70	4.50	7.8	0.8	6.4
5	C ₆ D ₆	10a	2.05	2.01	12.6	6.46	6.40	3.85	7.8	1.1	6.3
6	C ₆ D ₆	10b	2.10	1.89	12.5	6.48	6.39	4.01	7.7	0.8	6.5
7	C ₆ D ₆	10c	2.16	1.92	12.5	6.48	6.39	3.96	7.7	0.02	6.5
8	C ₆ D ₆	10d	2.10	2.06	12.7	6.46	6.35	3.98	7.8	1.0	6.4
9	CDCl ₃	11a	<i>2.31</i>	<i>1.95</i>	<i>12.7</i>	<i>6.83</i>	<i>6.56</i>	<i>4.29</i>	7.8	<i>0.7</i>	<i>6.0</i>
10	CDCl ₃	11b	<i>2.34</i>	<i>1.85</i>	<i>12.5</i>	<i>6.81</i>	<i>6.51</i>	<i>4.43</i>	7.9	<i>1.3</i>	<i>6.1</i>
11	CDCl ₃	11c	<i>2.36</i>	<i>1.85</i>	<i>12.5</i>	<i>6.78</i>	<i>6.50</i>	<i>4.40</i>	7.9	<i>0.7</i>	<i>6.0</i>
12	CDCl ₃	11d	<i>2.33</i>	<i>1.94</i>	<i>12.6</i>	<i>6.81</i>	<i>6.51</i>	<i>4.41</i>	7.8	<i>1.2</i>	<i>6.0</i>
13	C ₆ D ₆	11a	<i>2.29</i>	<i>1.79</i>	<i>12.5</i>	<i>6.52</i>	<i>6.11</i>	3.95	7.8		<i>6.0</i>
14	C ₆ D ₆	11b	<i>2.33</i>	<i>1.67</i>	<i>12.7</i>	<i>6.54</i>	<i>6.01</i>	4.05	7.8		<i>6.0</i>
15	C ₆ D ₆	11c		<i>1.74</i>	<i>12.7</i>		<i>6.01</i>	4.01	7.9		<i>6.0</i>
16	C ₆ D ₆	11d	<i>2.35</i>	<i>1.82</i>	<i>12.7</i>	<i>6.52</i>	<i>6.04</i>	4.03	7.8		<i>6.0</i>

Entries in normal type refer to spectra of isolated samples, entries in italic type to satellite spectra in spectrograms of the mother liquors of the main products **10**. Bold type: Signals selected for following the reactions by ^1H NMR.

The donor-*syn* geometry of these main adducts has been unambiguously established by single-crystal X-ray structure analyses for **10a**,³³ **10b**,³⁴ and **10c**.³⁵ Since the ^1H chemical shifts and the coupling constants for the 10-H₂ AB system and 2-H, 3-H, and 4-H of **10d** in both CDCl₃ and C₆D₆ solution matched very well those of **10a-c** (Table 1), a donor-*syn* geometry can safely be assumed as well for **10d**. Also, the ^{13}C chemical shifts of compounds **10a-d** are quite close (Table 2).

Table 2. $^{13}\text{C}\{^1\text{H}\}$ chemical shifts (δ/ppm) of photoproducts **10a-d** in CDCl_3

Comp.	Cycloamino methylene groups				Other carbon atoms				
	α	β	γ	δ	COCH_3	C-10	C-4	C-1	C-9
10a	48.9	23.3			28.9	42.0	48.5	59.2	66.0
10b	49.4	25.7	24.2		28.9	43.2	45.8	52.2	66.8
10c	50.1	26.2	27.2	28.1	28.8	43.4	47.4	59.1	67.6
10d	50.0	27.8	25.7	25.3	28.8	42.3	46.9	50.0	68.2

Comp.	Other carbon atoms (continued)									
	CN	C-5	C-6	C-7	C-8	C-2	C-3	C-4a	C-8a	C=O
10a	120.1	120.8	125.5	126.2	126.5	134.5	136.4	137.8	141.9	207.7
10b	119.4	120.8	125.6	126.2	126.4	134.5	137.0	137.1	142.0	207.8
10c	120.5	120.7	124.2	125.7	125.8	134.2	136.9	137.9	142.0	207.6
10d	121.1	128.0	125.7	125.9	126.5	134.0	137.3	137.5	141.4	207.7

The configuration of compounds **10** is also reflected in the 1D NOE intensity enhancements found for compound **10c** as an example (see Table 3). Especially the enhancement noted for the multiplet of the aromatic protons 5, 6, and 7 upon irradiation of the multiplet ascribed to the quasi-equatorial hexahydroazepin-1-yl α -protons indicates a *syn*-orientation of this cycloamino group to the benzenoid ring (entry 5). This effect requires a brief comment.

Table 3. 1D NOE intensity enhancements observed for compound **10c** in C_6D_6 (δ/ppm , assignments)

Entry	Signal irradiated ^a	Signals enhanced ^a
1	1.92 <i>10-H_B</i>	2.16 <i>10-H_A</i> ; 2.40-2.50 <i>N(CH_{qax})₂</i>
2	1.96 <i>COCH₃</i>	6.48 <i>2-H</i> ; 6.77 <i>8-H</i>
3	2.18 <i>10-H_A</i>	1.92 <i>10-H_B</i>
4	2.41-2.50 <i>N(CH_{qax})₂</i>	0.94-1.36 <i>(CH₂)₄</i> ; 1.92 <i>10-H_B</i> ; 2.50-2.60 <i>N(CH_{qeq})₂</i> ; 3.96 <i>4-H</i>
5	2.50-2.60 <i>N(CH_{qeq})₂</i>	0.96-1.34 <i>(CH₂)₄</i> ; 2.41-2.50 <i>N(CH_{qax})₂</i> ; 3.96 <i>4-H</i> , 6.82- 6.93 <i>5-, 6-, 7-H</i>
6	3.96 <i>4-H</i>	2.50-2.60 <i>N(CH_{qeq})₂</i> ; 6.39 <i>3-H</i>
7	6.39 <i>3-H</i>	3.96 <i>4-H</i>

^a *qax* = quasi-axial, *qeq* = quasi-equatorial

While the 1-piperidinyl α -protons in **10b** give rise to two distinct multiplets (in C_6D_6 at δ 2.20-2.30 and 2.42-2.55 ppm), the one at lower field was assigned to the equatorial, the one at higher field to the axial α -H-atoms.³⁶ Compounds **10a,c** in the same solvent show almost baseline separated $\text{N}(\text{CH}_2)_2$ multiplets, the branch of which at higher field being assignable to the

quasi-axial (qax), the branch at lower field to the quasi-equatorial (qeq) α -H-atoms. For **10d**, this near-splitting is observed only in CDCl_3 but not in C_6D_6 . For **10c**, separate irradiation of the qax and qeq α -proton signals gives different patterns of NOE enhancements (see Table 3, entries 4 and 5).

Identification of the byproducts

The mother liquor residues, when subjected to ^1H NMR investigation in freshly prepared CDCl_3 solution, did show, besides residual starting materials **1** and **9a-d**, additional (albeit partly resolved) signal sets for minor byproducts to which structures **11-13**, all being isomers of **10**, were assigned primarily on the basis of their ^1H NMR data as follows:

- For better resolution it had turned out to be advantageous to inspect also the ^1H NMR spectra of the mother liquor residues of **10a-d** in C_6D_6 as solvent.
- Two related signal sets were assigned to two 2-epimeric 1,2-[2+2]-adducts **12a-d** and **13a-d** each showing an AX system for the geminal protons at C-1, and two styrene-like olefinic protons coupled to a third one assigned to the bridgehead 2a-H (Table 4);
- A third signal set very similar to those of **10a-d**, except that the AB system of the latter ($\Delta\nu/J = 1-8$) had been replaced with a borderline AX pattern ($\Delta\nu/J = 8-12$ in CDCl_3 and 12-15 in C_6D_6), and two olefinic protons (2-H, 3-H), not conjugated to the benzenoid ring and both coupled to the bridgehead H-4 (Table 1, entries 9-12 and 13-16).
- Additionally, in separate experiments starting materials **1** and **9a,c** were irradiated deliberately to low conversion to obtain the well crystallizing byproducts **13a,c** preferentially, so their complete ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra could be obtained separately without overlap with signals from other products present.

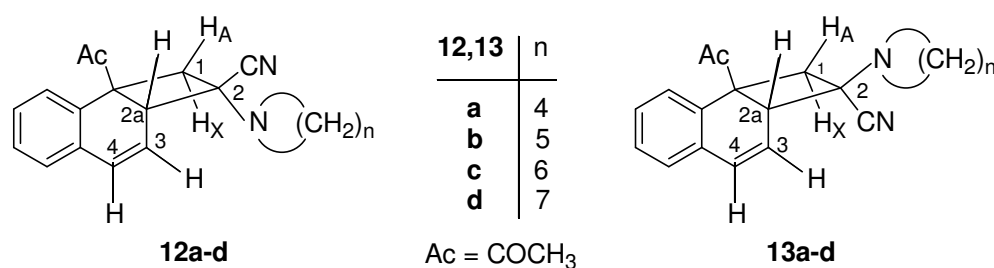
The configuration assignments of byproducts **12** and **13** were made as follows: from Table 4 the relevant chemical shifts in CDCl_3 (C_6D_6) for 1- H_A , 1- H_X and 2a-H can be taken as follows:

12c: 1- H_A 3.42 {3.41}, 1- H_X 2.41 {2.14}, 2a-H 3.64 {3.25} (entries 3 and 7)

13c: 1- H_A 3.25 {3.26}, 1- H_X 2.69 {2.48}, 2a-H 3.21 {2.92} (entries 11 and 15)

The *cis*-vicinal CN group deshields^{37,38} 1- H_A in **12c** (compared to that in **13c**) but 1- H_X in **13c** (compared to that in **12c**). In both compounds 1- H_X experiences a high field shift through the anisotropy of the benzenoid ring, this effect is, however, partially compensated by the influence of the *cis*-vicinal CN group in **13c** but not in **12c**. The latter group somewhat deshields 2a-H in **12c** but not in **13c**. These findings allow to discriminate between structures **12c** and **13c**.

For **13c**, also NOE's (Table 5) are in accord with the donor-*anti* geometry. Irradiation into the α -methylene multiplet (2.40-2.56 ppm) enhances not only the $(\text{CH}_2)_4$ multiplet but also the signals at 3.21 2a-H, 3.25 1- H_A , and 5.81 ppm 3-H. Further relevant effects (signal irradiated / signal enhanced): 2.69 1- H_X / 6.93 8-H; 3.21 2a-H / 5.81 3-H. In view of the very similar ^1H NMR data (see Table 4), compounds **13a,b,d** and **12a,b,d** may be assigned the donor-*anti* and donor-*syn* geometries, respectively.

Table 4. Structurally relevant 300.1 MHz ^1H NMR data of byproducts **12** and **13** (δ in ppm, J in Hz) as far as they could be extracted from the spectrograms

Entry	Solvent	Comp.	1- H_A	1- H_X	$ ^2J_{AX} $	2a-H	$^4J_{1A,2a}$	4-H	3-H	$^3J_{3,4}$	$^4J_{2a,4}$	$^3J_{2a,3}$
1	CDCl_3	12a	3.42		12.8			6.56	5.76	9.8	1.4	4.8
2		12b						6.58	5.74	10.0	1.9	4.3
3		12c	3.42	2.41	12.1	3.64		6.58	5.73	9.8		4.9
4		12d						6.58	5.78	10.3	1.1	4.9
5	C_6D_6	12a	3.57		12.3		2.0	6.16	5.30	9.9	1.6	4.9
6		12b						6.20	5.35	9.5	0.8	
7		12c	3.41	2.14	12.2	3.25	2.5	6.17	5.27	10.0	0.6	4.8
8		12d	3.46	2.11	12.3		2.3	6.15	5.28	9.7	1.1	5.1
9	CDCl_3	13a	3.35	2.70	14.5	3.32	0.8	6.71	5.82	9.8		5.7
10		13b	3.26	2.67	12.1	3.22		6.70	5.78	9.7		5.6
11		13c^a	3.25	2.69	12.0	3.21	0.7	6.69	5.81	9.8		5.7
12		13d						6.69	5.81	9.8		5.7
13	C_6D_6	13a	3.36	2.50	12.1	2.98	1.0	6.39	5.47	9.8	2.4	5.6
14		13b	3.28	2.47	12.0	2.86	0.6	6.38	5.36	9.7		5.6
15		13c	3.26	2.48	12.0	2.92	0.8	6.38	5.43	9.7		5.6
16		13d	3.33	2.46	12.2	2.98	0.8	6.38	5.47	9.8	2.1	5.5

Entries in normal type refer to spectra of isolated samples, entries in italic type to satellite spectra in spectrograms of the mother liquors of the main products **10**. Bold type: Signals selected for following the reactions by ^1H NMR.

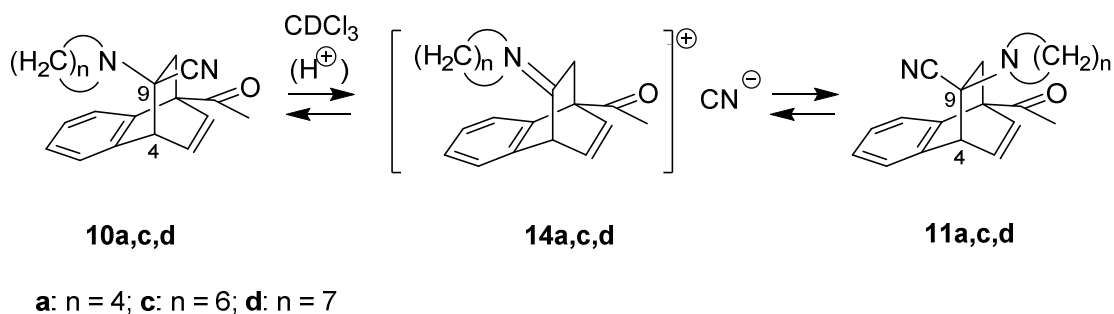
^a An additional coupling of $^4J_{1-H_X,2a} = 0.8$ Hz is observed.

Table 5. 1D NOE intensity enhancements observed for compound **13c** in CDCl₃ (δ /ppm, assignments)

Entry	Signal irradiated	Signals enhanced
1	1.52-1.73 (CH ₂) ₄	2.40-2.59 N(CH ₂) ₂ ; 3.21 2a-H
2	2.40-2.56 N(CH ₂) ₂	1.50-1.75 (CH ₂) ₄ ; 3.21 2a-H, 3.25 1-H _A ; 5.81 3-H
3	2.69 1-H _B	3.25 1-H _A ; 6.93 8-H
4	3.21 2a-H	2.40-2.59 N(CH ₂) ₂ ; 2.69 1-H _B ; 5.81 3-H
5	3.26 1-H _A	2.69 1-H _B

The close similarity of the third low intensity ¹H NMR signal set, especially the resonances for 10-H_AH_B and 2-H, 3-H, 4-H with those of the main products **10a-d**, suggested the third byproduct to be the 9-epimer **11a-d** of the latter. Compared with the situation in **10a-d**, the upfield shift exerted by the benzenoid ring on H_A is in part counterbalanced by the influence of the vicinal nitrile group, while the downfield shift of that group on 10-H_B in **10a-d** is no longer present in **11a-d**, thus 10-H_A resonates at lower and 10-H_B at slightly higher field than in the ¹H NMR of **10a-d**.

The following observation is noteworthy in this context: When CDCl₃ solutions of pure isolated **10a,c,d** (but not of **10b!**) were kept standing for periods between several days and a week, additional signal sets identical to those assigned to **11a,c,d** built up. This suggested that compounds **10a,c,d** underwent C9-epimerisation forming **11a,c,d** by opening and re-closure of either the C4-C9 bond or (probably catalyzed by traces of acid) the C9-CN bond generating the close ion pair **14** which, when at least partially separated, may return to either **10** or **11** (Scheme 5).

**Scheme 5**

Time dependent product distribution

Mode selectivity (i. e. 1,2- vs. 1,4-cycloaddition) had earlier been surmised to be time dependent for the photocycloadditions of several captodative alkenes to **1**.⁴ Since a related mode selectivity has been experimentally demonstrated for the photocycloaddition of 5-fluoro-1,3-dimethyluracil to naphthalene³⁹, and time dependent product ratios in intramolecular [2+2]-photocycloadditions of 2-alkenylsubstituted 1-naphthonitriles have been reported,⁴⁰ such time dependence studies were found desirable also for the photocycloadditions of **9a-d** to **1**. Thus, 5 mm (o.d.) NMR tubes were charged with 0.6 mL samples of C₆D₆ solutions 0.1 M in both **1** and **9a-d** and exposed to the same broad-band UV irradiation as used for the preparative scale runs. 300 MHz ¹H NMR spectra were scanned at appropriate regular time intervals and the concentrations of residual starting material **1** and the four cycloadducts **10**, **11**, **12**, and **13** were determined by signal intensity integration at selected chemical shifts (9.15 ppm for **1**, for products **10**, **11**, **12**, and **13** see Tables 1 and 4). Integrals were taken as measures of percentages and have not been calibrated. As in other studies applying the same NMR methodology, the experimental error is to be assumed as $\pm 1\%$ ⁴¹ or $\pm 1-2\%$.⁴² This error may significantly increase since the NMR integration method tends to overestimate the major diastereomer in a mixture when the *dr* is 100:1 or even larger.⁴² In spite of any experimental errors or methodological shortcomings, our experimental results suffice to show a clear trend. Since no further products were observed during the total time span of the experiments, the proportions of residual starting material **1** and products **10**, **11**, **12**, and **13** were expressed in % with the sum of all percentages of said components at any time regarded as 100%. Time-resolved concentration changes are shown in Figure 1 for the photocycloadditions of **9a-d** to **1**. For **9b** a separate determination for both 1,2- and both 1,4-adducts was impossible, thus only the sum of the percentages of the epimeric mixtures of the 1,4-adducts **10b,11b** and 1,2-adducts **12b,13b**, respectively, could be determined.

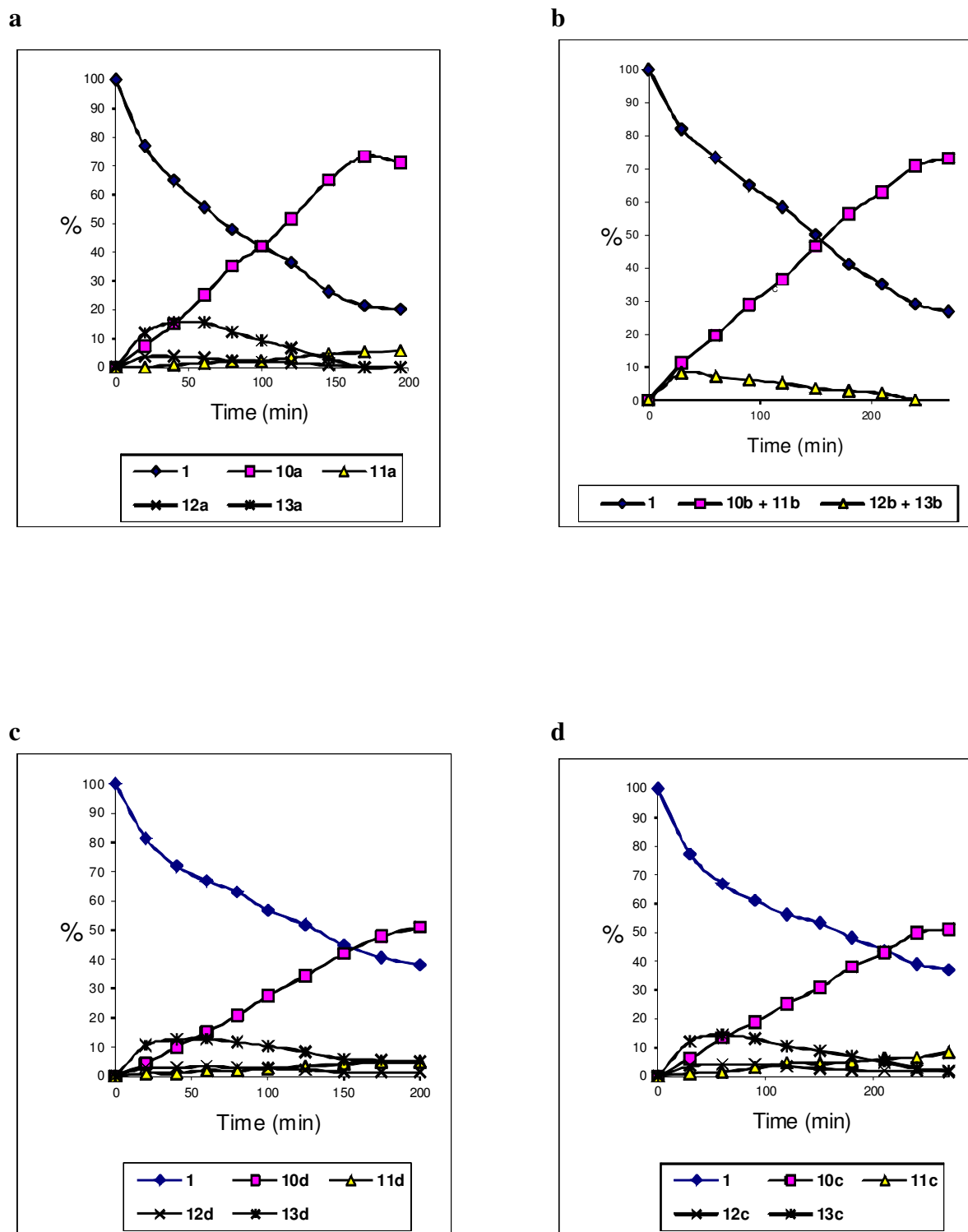


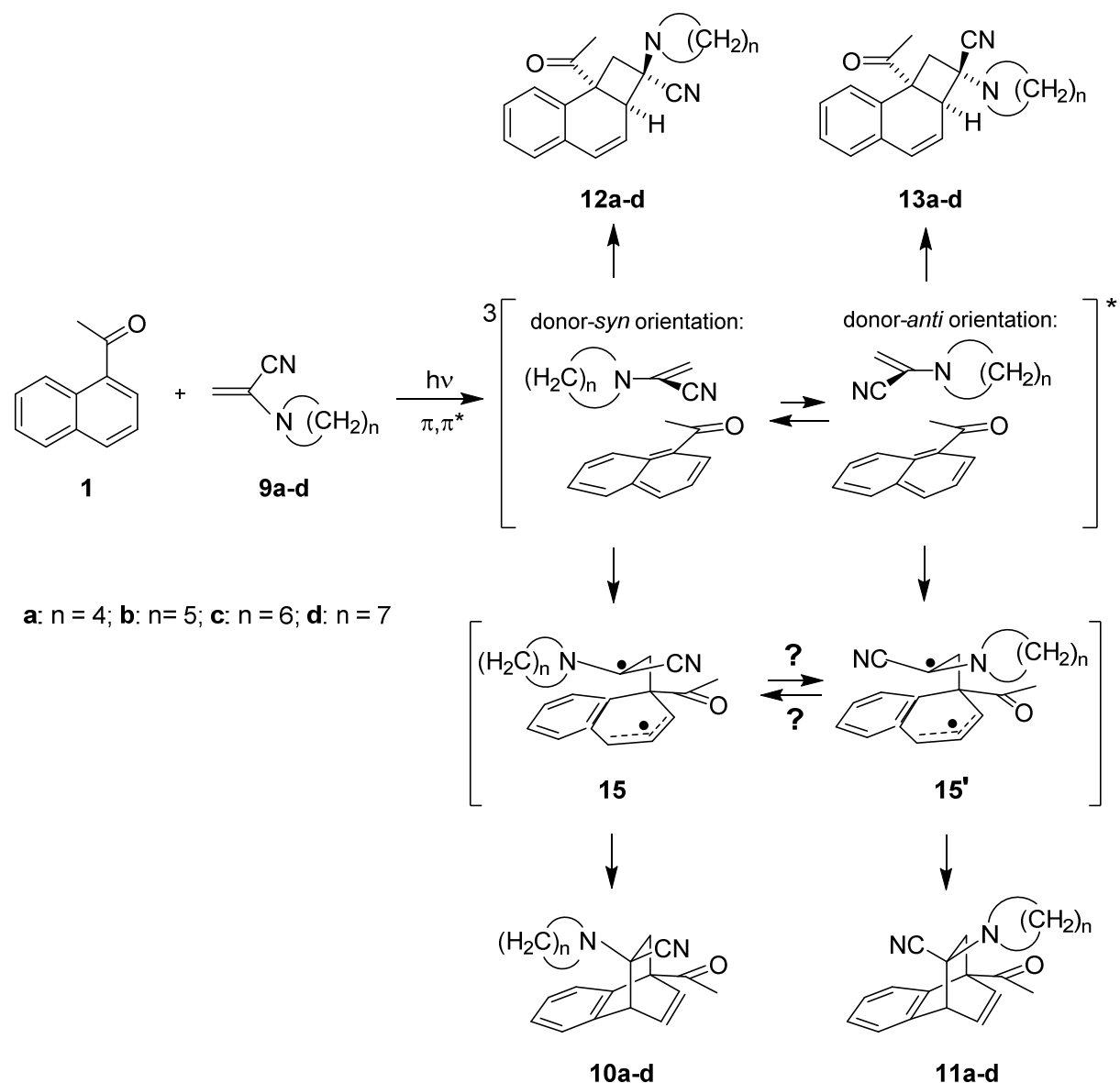
Figure 1. Small-scale irradiations of 1-acetonaphthone (**1**) in the presence of alkenes **9a** (a), **9b** (b), **9c** (c), and **9d** (d). The percentages of starting material **1** and products **10**, **11**, **12**, and **13** versus time were followed by ^1H NMR in C_6D_6 .

From Figure 1 it can be taken that the curves for both the epimeric 1,4-adducts **10a,c,d** (donor-*syn*) and **11a,c,d** (donor-*anti*) gradually climb although with clearly different slopes, whereas the plots for the 1,2-donor-*anti* products **13a,c,d** initially climb faster than those for the main products **10a,c,d** but go through a maximum after 50, 60, and 40 min, respectively, and have dropped to a few percent or close to zero at the end of the experiment. This clearly demonstrates the donor-*anti* 1,2-photocycloaddition forming **13a,c,d** to be faster by a factor of approximately 1.9, 2.4, and 2.7, respectively, at low conversion and that the 1,4-photocycloadducts **10**, **11** are formed independently of the 1,2-photoadducts **12**, **13** and not consecutively from these.

The reason for this is to be sought in the enhanced light sensitivity of the 1,2-cycloadducts **12**, **13** with their styrene-like chromophore which causes their photo-retro-cleavage to the starting materials, while the 1,4-photocycloadducts **10** and **11** remain stable towards the incident light and accumulate. Reversibility of intramolecular [2+2]-photocycloadditions of double bonds to the 1-cyanonaphthalene system, preceding the [3+2]-photocycloaddition, have also been observed by Mizuno et al.^{22,23}

The course of the observed photocycloadditions

Monochromatic (313 nm) excitation of a common equimolar solution of **1** and model compound **2** in acetonitrile had shown a marked decrease of the absorbance between 250 and 290 nm and no isosbestic points over the wavelength range 240-380 nm in the reaction spectrum, demonstrating that only products of lower absorbance than that of either starting material are produced. The graphical evaluation of the reaction spectrum gave linear absorbancy-time and absorbancy diagrams⁴³. These findings point to a simple reaction of the type $A + B \rightarrow C$ (or several parallel reactions of that type).



Scheme 6

Aspects of regio- and stereoselection (facial selectivity) have been discussed before^{4,7,14} and will be addressed here only briefly (Scheme 6). In both of the parallel reaction modes ([2+2]- and [4+2]-photocycloadditions) two relative orientations (donor-*syn* and donor-*anti*) of the reactants determine the stereochemical outcome and are apparently maintained all the way to the final products **10-13**. Whether or not triplet excitation of **1** is followed by formation of a (even very short lived) exciplex, in turn followed by formation of a biradical, cannot be answered yet. The only transient observed in a ns-laser flash photolysis experiment (308 nm excimer laser of 7 ns pulse width and 10 mJ energy) with **1** in the presence of model compound **2** in acetonitrile and with **9a-c** in methanol is the first excited (π, π^*) triplet state of **1** which is quenched by **2**, **9a-c**,

TMDD and also by methyl viologen (MV^{++})⁸. The latter reagent allows to detect biradicals indirectly⁴⁴ but no such biradical could be detected either spectroscopically or by quenching.

Indeed biradicals like **15/15'** with one captodatively¹⁻³ substituted and one benzylic/allylic terminus are attractive intermediates at least in the [4+2]-photocycloaddition but still have to be regarded as speculative. Because of their likely fleeting existence it is doubtful that they interconvert by rotation around the C9-C10 bond, since products **10** and **11** cannot be interconverted thermally and there are no direct interconversions of [2+2]- and [4+2]-photoadducts either. All photoproducts decay to starting materials upon thermal activation.

A direct photointerconversion of products **12/13** to **10/11** may be ruled out by analogy to the photochemical behavior of the model compound **4**⁷ (see Scheme 1). When irradiated (313 nm) in acetonitrile solution, **4** is completely decomposed into **1** and **2** as demonstrated by the rapid increase of absorbance of the solution prior to a slow but marked decrease when the [4+2] photocycloadduct is formed. If **4** had been transformed directly into **3**, the absorbance of the solution had to decrease from the beginning of the experiment.

The finding that acidic impurities in $CDCl_3$ may catalyze the conversion of **10a,c,d** into **11a,c,d** at ambient temperature (Scheme 5) does not require biradical intermediates. This transformation, however, indicates that compounds **11** are thermodynamically more stable than their 9-epimers **10**.

Conclusions

Photoexcited 1-acetonaphthone (**1**) adds a series of α -cyanoenamines **9a-d** in two parallel reaction modes, namely, the 1,4-[4+2]- and the 1,2-[2+2]-addition. Since in either case a mixture of two epimers is formed, a total of four independent cycloadditions is taking place. As can be seen at low conversion, the order of rate of these is: 1,2 donor-*anti* (leading to **13**) > 1,4 donor-*syn* (leading to **10**) > 1,2 donor-*syn* (leading to **12**) > 1,4 donor-*anti* (leading to **11**). While the main products isolated in 60-85% yield from preparative scale irradiations reaching 42-45% conversion of starting material **1** are the donor-*syn* 1,4-[4+2]-cycloadducts **10a-d**, their 9-epimeric donor-*anti* 1,4-[4+2]-cycloadducts have been identified by ¹H NMR spectroscopy only to be present in 3% (**11a**), 6% (**11c**), and 4% (**11d**) in the crude photolysates. The donor-*anti* 1,2-[2+2]-photocycloadducts **13a,c,d** are noteworthy since they are at low conversion present in the reaction mixtures in significantly higher concentrations than those of the main photoadducts **10a,c,d**, but later, as the screening effect of the starting material **1** decreases, undergo light induced cleavage back to the starting materials, while the concentrations of both 1,4-photocycloadducts **10** and **11** increase. While only two (**13a,c**) of the donor-*anti* [2+2]-cycloadducts **13** could be isolated and their structures unambiguously be determined, byproducts **12a-d** and **13b,d** could be identified from their individual ¹H NMR signal sets only. Any distinct differences in mode or stereoselectivity in the photocycloadditions of **9a-d** to **1**, dependent on the

ring size of the donor group of **9**, have not been observed, however. Just gradual differences could be detected by ^1H NMR-following of the photocycloadditions.

Experimental Section

General. Mps have been determined on a Kofler hot stage microscope. – IR spectra have been recorded from liquid films or KBr disks on a Perkin-Elmer 983 spectrophotometer. – Mass spectrometry: An AMD 604 instrument (EI mode) using 70 eV ionization energy and a direct inlet system, adjusted to the temperatures given, was used. – NMR spectra were recorded on a Bruker WM 300 instrument operating at 300.1 MHz for ^1H and 75.5 MHz for ^{13}C , with TMS as internal standard. Abbreviations: s singlet, d doublet, m multiplet. – UV spectra were taken on a Perkin Elmer Lambda 40 instrument. – Elemental analyses for C, H, and N were obtained on a Carlo Erba Elemental Analyzer model 1106.

1-Acetonaphthone (1) was purchased from Aldrich and distilled, bp 75-80 °C /0.15 Torr. ^1H NMR (300.1 MHz, CDCl_3): δ_{H} 2.70 (3H, s, COCH_3), 7.30-8.90 (7 H_{arom} , several m, 7CH); (300.1 MHz, C_6D_6): δ_{H} 2.23 (3H, s, COCH_3), 7.01-7.61 (6 H_{arom} , m, 2-H to 7-H), 9.16-9.19 (1 H_{arom} , m, 8-H). UV [cyclohexane; λ_{max} , nm, (log ϵ): 211 (4.59), 2.16 (4.56), 235 (4.23), 245 (4.21), 302 (3.81), 322 (3.60). – **2-(Cycloamino)propenenitriles 9a-d** were prepared as described earlier⁴⁵ by adaption of the procedure for preparation of **2** published by Temin⁵ to prepare **9a**, and the procedure for preparation of **9b** by Balsubramanian et al.⁴⁶ was used to prepare **9b-d**. All samples were refined by bulb-to-bulb distillation *in vacuo*. IR (liquid film), 300.1 MHz ^1H NMR (CDCl_3) and 75.5 MHz $^{13}\text{C}\{1\text{H}\}$ NMR (CDCl_3) data have already been given in ref.⁴⁷, and only additional physical, spectral, and analytical data are given below.

2-(1-Pyrrolidinyl)propenenitrile (9a). Bp 31 °C/0.4 Torr, lit.⁴⁷ 58-59 °C/1.5 Torr, n_{D}^{20} = 1.4995. UV [cyclohexane; λ_{max} , nm (log ϵ): 264 (3.94). ^1H NMR (300.1 MHz, C_6D_6): δ_{H} 1.14-1.21 [4H, m, $(\text{CH}_2)_2$], 2.59-2.65 [4H, m, $\text{N}(\text{CH}_2)_2$], 3.77 and 4.32 (1H each, no coupling observed, 3- H_2). MS (22 °C) m/z (%) = 122 (M, 96), 121(91), 94 (100), 93 (38). Anal. Calcd for $\text{C}_7\text{H}_{10}\text{N}_2$ (122.17): C, 68.82; H, 8.25; N, 22.93%. Found: C, 69.06; H, 8.32; N, 22.82%.

2-(1-Piperidinyl)propenenitrile (9b). Bp 42 °C/0.026 Torr, lit.⁴⁶ 100 °C/2 Torr, lit.⁴⁷ 77 °C/1.5 Torr, n_{D}^{20} 1.4038. UV [cyclohexane; λ_{max} , nm (log ϵ): 259 (3.79). ^1H NMR (300.1 MHz, C_6D_6): δ_{H} 0.95-1.22 [6H, m, $(\text{CH}_2)_3$], 2.48-2.57 [4H, m, $\text{N}(\text{CH}_2)_2$], 3.77 (1H, d, $^2J_{\text{HH}}$ 1.63 Hz, 3- H_B), 4.19 (1H, d, $^2J_{\text{HH}}$ 1.63 Hz, 3- H_A). MS (124 °C), m/z (%) = 136 (M, 100), 121 (29), 108 (29), 95 (33). Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_2$ (136.20): C, 70.55; H, 8.88; N, 20.57%. Found: C, 70.51; H, 8.93; N, 20.64%.

2-(Hexahydro-1H-azepin-1-yl)propenenitrile (9c). Bp 70 °C/0.038 Torr.⁴⁵ UV [cyclohexane; λ_{max} , nm (log ϵ): 270 (3.78). ^1H NMR (300.1 MHz, C_6D_6): δ_{H} 1.08-1.16 [4H, m, $(\text{CH}_2)_2$], 1.20-1.30 [4H, m, $(\text{CH}_2)_2$], 2.75-2.83 [4H, m, $\text{N}(\text{CH}_2)_2$], 3.86 (1H, d, $^2J_{\text{HH}}$ 1.62 Hz, 3- H_B), 4.29 (1H, d, $^2J_{\text{HH}}$ 1.62 Hz, 3- H_A). MS (137 °C), m/z (%) = 150 (M, 100), 135 (56), 121 (30), 110 (24), 107

(54), 95 (47). Anal. Calcd for C₉H₁₄N₂ (150.23): C, 71.96; H, 9.39; N, 18.65%. Found: C, 72.04; H, 9.38; N, 18.79%.

2-(Octahydroazocin-1-yl)propenenitrile (9d). Bp 53 °C/0.032 Torr⁴⁵. UV [cyclohexane; λ_{max}, nm (log ε)]: 273 (3.95). ¹H NMR (300.1 MHz, C₆D₆): δ_H 1.10-1.35 [10H, m, (CH₂)₅], 2.55-2.62 [4H, m, N(CH₂)₂], 3.86 (1H, d, |²J_{HH}| 1.59 Hz, 3-H_B), 4.31 (1H, d, |²J_{HH}| 1.59 Hz, 3-H_A). MS, *m/z* = 164 (M, 100), 149 (48), 135 (20), 121 (42), 110 (18), 107 (37, 96 (72), 95 (62). Anal. Calcd for C₁₀H₁₆ N₂ (164.25): C, 73.13; H, 9.82; N, 17.06%. Found: C, 72.90; H, 9.96; N, 16.94%.

Preparative scale irradiations

A Philips HPK 125 W high pressure mercury lamp was used in connection with a water-cooled Duran™ immersion well (λ > 280 nm) and a cylindrical vessel with a gas in- and outlet and a magnetic stirrer. Cyclohexane solutions (170 mL) of 1-acetonaphthone (**1**) and alkene **9a-d** (0.1 M each) were purged with Ar (99.996%) for 30 min and then irradiated for the periods given with stirring and under continuous Ar purging (for details see Table 6) whereby the mixture assumed a yellow or orange-brown color. The photolyzates were concentrated to oily residues which were diluted with hexane and stirred vigorously under ice cooling. The crude precipitates were filtered off, washed with hexane and dried. Crystallization from ethyl acetate/hexane (1:1) under ice/salt cooling gave the refined products **10a-d** (see Table 6 for yields). Structurally relevant ¹H NMR data have been given in Tables 1 and 4, ¹³C{¹H} NMR data in Table 2.

Table 6. Preparative photocycloadditions of alkenes **9a-d** (1.7 mmol each) to 1-acetonaphthone (**1**, 2.89 g, 1.7 mmol) in 170 ml of cyclohexane. Conditions and yields

Alkene used (g)	Irradiation time / h	Conversion of 1 / %	Product	Crude yield* g (%)	Refined yield* g (%)
9a (2.07)	9	44	10a	1.87 (85)	1.30 (60)
9b (2.31)	8	42	10b	1.74 (80)	1.33 (61)
9c (2.55)	20	45	10c	2.29 (93)	1.65 (67)
9d (2.79)	18	45	10d	2.49 (96)	2.16 (85)

*Yields refer to converted starting material **1**.

Filtrates and washings were concentrated to dryness and subjected to ¹H NMR analysis (in CDCl₃ solution) which revealed the presence of a 1:1 mixture of both starting materials, the concentrations of which were determined by signal integration and allowed the determination of conversion of **1**, on which the yields given in Table 6 are based. In addition to the signals of the main products **10**, three minor signal sets were detected and assigned to the minor byproducts **11a-d** (see Table 1, entries 9-16), **12a-d** (Table 4, entries 1-8) and **13a-d** (Table 4, entries 9-16).

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-pyrrolidiny)-1,4-ethanonaphthalene-9-carbonitrile (10a). Mp 108 °C (decomp.). IR (ν̄/cm⁻¹): 2212 (CN), 1712 (C=O). UV [acetonitrile, λ_{max}, nm (log ε)]: 256 (2.34), 262 (2.39), 270 (2.26). ¹H NMR (300.1 MHz, CDCl₃

{C₆D₆}: See Table 1, entries 1 and 5, and δ_{H} 1.62-1.75 {1.16-1.36} (4H, m, pyrrolidinyl β -H), 2.51 {1.95} (3H, s, COCH₃), 2.60-2.72 {2.30-2.41} [2H, m, N(CH_{qax})₂], 2.72-2.84 {2.46-2.60} [2H, m, N(CH_{req})₂], 6.92-7.00 {6.73-6.79} (1H_{arom}, m, 8-H), 7.15-7.32 {6.79-6.94} (3H_{arom}, m, 5-H, 6-H, 7-H). MS (95 °C), m/z (%) = 265 (M-HCN, 10), 221 (M-HCN and COCH₃, 5), 170 (C₁₂H₁₀O **1**, 40), 155 (C₁₁H₇O, 67), 122 (**9a**, 100). Anal. Calcd for C₁₉H₂₀N₂O (292.38): C, 78.05; H, 6.90; N, 9.58%. Found: C, 78.02; H, 6.88; N, 9.54%.

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-piperidinyl)-1,4-ethanonaphthalene-9-carbonitrile (10b). Mp 143-144 °C (decomp.). IR ($\tilde{\nu}/\text{cm}^{-1}$): 2216 (CN), 1700 (C=O). UV [acetonitrile, λ_{max} , nm (log ϵ): 256 (2.30), 262 (2.36), 270 (2.20)]. ¹H NMR (300.1 MHz, CDCl₃ {C₆D₆}: See Table 1, entries 2 and 6, and δ_{H} 1.30-1.51 {1.01-1.19} (6H, m, piperidinyl β - and γ -H), 2.52 {1.94} (3H, s, COCH₃), 2.40-2.50 {2.20-2.30} [2H, m, N(CH_{ax})₂], 2.62-2.75 {2.42-2.55} [2H, m, N(CH_{eq})₂], 6.94-6.97 {6.71-6.77} (1H_{arom}, m, 8-H), 7.15-7.26 {6.77-6.94} (3H_{arom}, m, 5-H, 6-H, 7-H). MS (125 °C.), m/z (%) = 279 (M-HCN, 8), 2.63 (M-COCH₃, 4), 236 (M-HCN and COCH₃, 4), 170 (C₁₂H₁₀O **1**, 40), 155 (C₁₁H₇O, 43), 136 (**9b**, 100). Anal. Calcd for C₂₀H₂₂N₂O (306.41): C, 78.40; H, 7.24; N, 9.14%. Found: C, 78.44; H, 7.21; N, 9.06%.

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-hexahydro-1H-azepin-1-yl)-1,4-ethanonaphthalene-9-carbonitrile (10c). Mp 91-92 °C (decomp.). IR ($\tilde{\nu}/\text{cm}^{-1}$): 2212 (CN), 1712 (C=O). UV [acetonitrile, λ_{max} , nm (log ϵ): 255 (2.46), 262 (2.48), 270 (2.36)]. ¹H NMR (300.1 MHz, CDCl₃ {C₆D₆}: See Table 1, entries 3 and 7, and δ_{H} 1.12-1.73 {0.94-1.36} (8H, m, hexahydro-1H-azepin-1-yl β - and γ -H), 2.51 {1.96} (3H, s, COCH₃), 2.55-2.70 {2.41-2.50} [2H, m, n(CH_{qax})₂], 2.70-2.92 {2.50-2.60} [2H, m, N(CH_{req})₂], 6.93-6.99 {6.75-6.78} (1H_{arom}, m, 8-H), 7.14-7.30 {6.83-6.94} (3H_{arom}, m, 5-H, 6-H, 7-H). MS (92 °C.), m/z (%) = 293 (M-HCN, 2), 2.63 (M-COCH₃, 0.4), 250 (M-HCN and COCH₃, 1), 170 (C₁₂H₁₀O **1**, 62), 155 (C₁₁H₇O, 99), 150 (**9c**, 47), 127 (C₁₀H₇, 100). Anal. Calcd for C₂₁H₂₄N₂O (320.44): C, 78.71; H, 7.55; N, 8.74%. Found: C, 78.51; H, 7.56; N, 8.62%.

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(octahydroazocin-1-yl)-1,4-ethanonaphthalene-9-carbonitrile (10d). Mp 103 °C (decomp.). IR ($\tilde{\nu}/\text{cm}^{-1}$): 2213 (CN), 1710 (C=O). UV [acetonitrile, λ_{max} , nm (log ϵ): 255 (2.40), 262 (2.40), 270 (2.25)]. ¹H NMR (300.1 MHz, CDCl₃ {C₆D₆}: See Table 1, entries 4 and 8, and δ_{H} 0.86-0.96, 1.08-1.32, 1.32-1.56 [2H, 4H, 4H 3m, (CH₂)₅ but {0.84-1.25} [10H, m, (CH₂)₅] -1.23}, 2.51 {1.94} (3H, s, COCH₃), 2.55-2.65 [2H, m, N(CH_{qax})₂] and 2.65-2.80 [2H, m, N(CH_{req})₂] but {2.36-2.51} [4H, m, N(CH₂)₂], 6.93-7.00 {6.72-6.78} (1H_{arom}, m, 8-H), 7.14-7.34 {6.82-6.95} (3H_{arom}, m, 5-H, 6-H, 7-H). MS (95 °C.), m/z (%) = 307 (M-HCN, 0.2), 2.64 (M-HCN and COCH₃, 0.2), 170 (C₁₂H₁₀O **1**, 95), 164 (**9d**, 31), 155 (C₁₁H₇O, 100), 127 (C₁₀H₇, 100). Anal. Calcd for C₂₂H₂₆N₂O (334.46): C, 79.00; H, 7.84; N, 8.38%. Found: C, 78.92; H, 7.88; N, 8.32%.

rel-(2R,2aR,8bS)-8b-Acetyl-2-(1-pyrrolidinyl)-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2-carbonitrile (13a). A solution of 2.55 g (15 mmol) of **1** and 1.87 g (15 mmol) of **9a** in 125 mL of cyclohexane was purged with Ar and irradiated as described above for 6.5 h to 23% conversion, A crop of 640 mg (23%, based on consumed starting material as are the following yields) of **10a** was directly filtered off and crystallized from ethyl acetate/hexane to give 490 mg

(48%), mp 108 °C (with decomp.). The original filtrate, combined with the mother liquor, gave 3.50 g of a residue which was subjected to preparative layer chromatography using hexane. Besides unreacted starting materials, from a zone at R_f 0.43, 90 mg of crystals were obtained and crystallized from ethyl acetate/hexane, yielding 74 mg (7%), mp 138-140 °C. IR ($\tilde{\nu}/\text{cm}^{-1}$): 2200 (CN), 1705 (C=O). UV [cyclohexane, λ_{max} , nm (log ϵ): 265 (3.77), 274 (3.77), 292 (3.37), 302 (3.29). ^1H NMR (300.1 MHz, CDCl_3): See Table 3, entry 9, and δ_{H} 1.76-1.87 [4H, m, $(\text{CH}_2)_2$], 2.01 (3H, s, COCH_3), 2.50-2.62 [4H, m, $\text{N}(\text{CH}_2)_2$], 6.91-6.96 (1H_{arom} , m 8-H), 7.11-7.28 (3H_{arom} , m, 5-H, 6-H, 7-H). MS (81 °C), m/z (%) = 265 (M-HCN, 1), 249 (M- COCH_3 , 3), 247 (5), 170 ($\text{C}_{12}\text{H}_{10}\text{O}$ **1**, 6), 155 ($\text{C}_{11}\text{H}_7\text{O}$, 17), 141 (5), 127 (17), 122 (**9a**, 100), 121 (10). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ (292.38): C, 78.05; H, 6.90; N, 9.58%. Found: C, 77.99; H, 6.71; N, 9.58%.

rel-(2R,2aR,8bS)-8b-Acetyl-2-(hexahydro-1H-azepin-1-yl)-1,2,2a,8b-tetrahydrocyclobuta[a]-naphthalene-2-carbonitrile (13c). A solution of 1.70 g (10 mmol) of **1** and 1.50 g (10 mmol) of **9c** in 100 mL of dry cyclohexane was purged with and irradiated under argon as described above for 4.5 h. After concentration, the residue was taken up in 50 mL of hexane and left standing at -70 °C for seven days. The crystalline precipitate was washed with cold isopropanol, dried and then taken up in 1 mL of ethyl acetate to which 20 mL of hexane were added. The mixture was left at -70 °C over night to give 90 mg of colorless crystals, mp 132 °C. IR ($\tilde{\nu}/\text{cm}^{-1}$): 2208 (CN), 1706 (C=O). UV [acetonitrile; $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 224 (4.50), 267 (3.96), 308 (plateau, 3.39). ^1H NMR (300.1 MHz, CDCl_3): See Table 3, entry 11, and δ_{H} 1.50-1.75 (8H, m, hexahydro-1H-azepin-1-yl β - and γ -H), 2.01 (s, 3H, COCH_3), 2.40-2.59 [m, 4H, $\text{N}(\text{CH}_2)_2$], 6.91-6.94 (1H, m, 8-H), 7.05-7.25 (3H_{arom} , m, 5-H, 6-H, 7-H). – ^{13}C NMR (75.5 MHz, CDCl_3): δ_{C} 24.9 (CH_3), 26.4 (2 CH_2), 28.7 (2 CH_2), 43.8 (C-1), 47.3 (C-8b), 47.5 (C-2a), 50.0 [$\text{N}(\text{CH}_2)_2$], 64.0 (C-2), 118.0 (CN); aryl and alkenyl CH at 121.2, 126.8, 128.6, 128.7, 129.3, 1131.1; quaternary aryl C at 131.5, 133.1; 205.4 (C=O). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}$ (320.4): C, 78.71; H, 7.55; N, 8.74 %. Found: C, 78.71; H, 7.52; N, 8.70%. A crop of 1.14 g of **1** was recovered chromatographically, thus a maximum of 0.56g (33%) of **1** had reacted.

Time dependent product distribution

In four separate experiments, solutions (6 mL each) 0.1 M in both 1-acetonaphthone (**1**) and either **9a**, **9b**, **9c** or **9d** in C_6D_6 , were purged for 30 min with Ar and equally distributed under Ar on ten NMR tubes (0.5 cm o. d.). The tubes were tightly stoppered, one was set aside as a blank, the other nine were affixed to the outer wall of a water-cooled immersion well and irradiated ($\lambda > 280$ nm), while being externally cooled with water, with a Philips 125 W high pressure mercury lamp. At regular time intervals a sample was scanned at 300.1 MHz. The integrals at δ 9.15 ppm (for **1**) and at selected δ values for the four products (see bold face entries in Tables 1 and 3) were added and the sum was taken as 100%, and the percentages of **1**, **10**, **11**, **12**, and **13** were calculated from the integrals and plotted (see Figure 1).

Acknowledgements

Support of our work by *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* is gratefully acknowledged. The authors are indebted to Prof. G. Gauglitz, Tübingen, for his experimental support in the stationary UV experiments.

References

1. Viehe, H.-G.; Janousek, Z.; Merényi, R. *Acc. Chem. Res.* **1985**, *18*, 148-154, and refs. cited therein.
<http://dx.doi.org/10.1021/ar00113a004>
2. Viehe, H.-G.; Merényi, R.; Janousek, Z. *Pure Appl. Chem.* **1988**, *60*, 1635-1644, and refs. cited therein.
<http://dx.doi.org/10.1351/pac198860111635>
3. Sustmann, R.; Müller, W.; Mignani, S.; Merényi, R.; Janousek, Z.; Viehe, H. G. *New J. Chem.* **1989**, *13*, 557-563.
4. Döpp, D., In *Organic, Physical and Materials Photochemistry (Molecular and Supramolecular Photochemistry, Vol. 6)* Ramamurthy, V.; Schanze, K., Eds., Marcel Dekker, New York, 2000; pp 101-148.
5. Temin, S. C. *J. Org. Chem.* **1957**, *22*, 1714-1715.
<http://dx.doi.org/10.1021/jo01363a619>
6. Döpp, D.; Krüger, C.; Memarian, H. R.; Tsay, Y. H. *Angew. Chem.* **1985**, *97*, 1059-1060.
<http://dx.doi.org/10.1002/ange.19850971219>
Döpp, D.; Krüger, C.; Memarian, H. R.; Tsay, Y. H. *Angew. Chem. Intl. Ed.* **1985**, *24*, 1048-1049.
<http://dx.doi.org/10.1002/anie.198510481>
7. Döpp, D.; Memarian, H. R. *Chem. Ber.* **1990**, *123*, 315-319.
<http://dx.doi.org/10.1002/cber.19901230216>
8. Döpp, D.; Memarian, H. R.; van Eijk, A. M. J.; Varma, C. A. G. O. *J. Photochem. Photobiol. A: Chem.* **1990**, *53*, 59-67.
[http://dx.doi.org/10.1016/1010-6030\(90\)87113P](http://dx.doi.org/10.1016/1010-6030(90)87113P)
9. Memarian, H. R.; Nasr-Esfahani, M.; Görner, H.; Döpp, D. *Indian J. Chem.* **2001**, *40B*, 1187-1190.
10. McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811-860.
<http://dx.doi.org/10.1021/cr00080a008>
11. Mizuno, K.; Maeda, H.; Sugimoto, A.; Chiyonobu, K. In *Understanding and Manipulating Excited State Processes (Molecular and Supramolecular Photochemistry, Vol. 8)*, Ramamurthy, V.; Schanze, K., Eds., M. Dekker: New York, 2001; p 127-241, and refs. cited therein.
12. Döpp, D.; Erian, A. W.; Henkel, G. *Chem. Ber.* **1993**, *126*, 239-242.

- <http://dx.doi.org/10.1002/cber.19931260132>
13. Döpp, D.; Jung, A. *Acta Chim. Slov.* **2009**, *56*, 664-668.
<http://acta.chem-soc.si/56/56-03-664.pdf>
14. Memarian, H. R.; Nasr-Esfahani, M.; Boese, R.; Döpp, D. *Liebigs Ann. Chem./Receil* **1997**, 1023-1027.
<http://dx.doi.org/10.1002/jlac.199719970535>
15. Memarian, H. R.; Nasr-Esfahani, M.; Döpp, D. *New. J. Chem.* **2001**, *25*, 476-478.
<http://dx.doi.org/10.1039/b006835g>
16. Memarian, H. R.; Nasr-Esfahani, M.; Döpp, D. *New. J. Chem.* **2001**, *25*, 1605-1609.
<http://dx.doi.org/10.1039/b105445g>
17. Mattay, J. *Angew. Chem.* **2007**, *119*, 674-677.
<http://dx.doi.org/10.1002/ange.200603337>
Mattay, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 663-665.
<http://dx.doi.org/10.1002/anie.200603337>
18. Hoffmann, N. *Synthesis* **2004**, 481-495.
<http://dx.doi.org/10.1055/s-2004-815973>
19. Bryce-Smith, D.; Gilbert, A.; Orger, B. H. *Chem. Commun.* **1966**, 512-514.
<http://dx.doi.org/10.1039/C19660000512>
20. Inoue, Y.; Nishida, K.; Ishibe, K.; Hakushi, T.; Turro, N. J. *Chem. Lett.* **1982**, 472-474.
21. Zupancic, N.; Sket, B. *J. Chem. Soc., Perkin Trans. 1* **1992**, 179-180.
<http://dx.doi.org/10.1039/P19920000179>
22. Mukae, H.; Maeda, H.; Mizuno, K. *Angew. Chem.* **2006**, *118*, 6708-6710.
<http://dx.doi.org/10.1002/ange.200602553>
Mukae, H.; Maeda, H.; Mizuno, K. *Angew. Chem. Intl. Ed.* **2006**, *45*, 6558-6560.
<http://dx.doi.org/10.1002/anie.200602553>
23. Mukae, H. Maeda, H.; Nashihara, S.; Mizuno, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1157-1161.
<http://dx.doi.org/10.1246/bcsj.80.1157>
24. Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065-3112.
<http://dx.doi.org/10.1021/cr910109c>
25. Kubo, Y.; Adachi, T.; Miyahara, N.; Nakayima, S.; Inamura, I. *Tetrahedron Lett.* **1998**, *39*, 9477-9480.
[http://dx.doi.org/10.1016/S0040-4039\(98\)02149-2](http://dx.doi.org/10.1016/S0040-4039(98)02149-2)
26. Kubo, Y.; Inoue, T.; Sakai, H. *J. Am. Chem. Soc.* **1992**, *114*, 7660-7663 and later papers by this group.
<http://dx.doi.org/10.1021/ja00046a009>
27. Griesbeck, A. G. "Photocycloaddition of Alkenes to Excited Carbonyl Compounds" in "Synthetic Organic Photochemistry", Griesbeck, A. G., Mattay, J. Eds. Volume 12 of "Molecular and Supramolecular Photochemistry", Ramamurthy, V. and Schanze, K. S. Eds. M. Dekker: New York, 2000; pp 89-139.
28. Döpp, D.; Pies, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1734-1735.

- <http://dx.doi.org/10.1039/C39870001734>
29. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd. Edn., CRC and Taylor & Francis, Boca Raton, London, New York, 2006; p 182.
30. Tam, J. N. S.; Yip, R. W.; Chow, Y. L. *J. Am. Chem. Soc.* **1974**, *96*, 4543-4549.
<http://dx.doi.org/10.1021/ja00821a030>
31. Singh, P.; Boocock, D. G. B.; Ullman, E. F. *Tetrahedron Lett.* **1971**, *12*, 3935-3936.
[http://dx.doi.org/10.1016/S0040-4039\(01\)97328-9](http://dx.doi.org/10.1016/S0040-4039(01)97328-9)
32. Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077-5078.
<http://dx.doi.org/10.1021/ja00769a048>
33. Döpp, D.; Kruse, C.; Flörke, U.; Henkel, G. *Acta Cryst. E* **2006**, *62E*, o3245-o3246.
<http://dx.doi.org/10.1107/S1600536806025876>
34. Döpp, D.; Kruse, C.; Flörke, U.; Henkel, G. *Acta Cryst. E* **2006**, *62E*, o3904-o3906.
<http://dx.doi.org/10.1107/S160053680603203X>
35. Döpp, D.; Kruse, C.; Flörke, U.; Henkel, G. *Acta Cryst. E* **2006**, *62E*, o3735-o3736.
<http://dx.doi.org/10.1107/S1600536806030571>
36. Crabb, T. A., Katritzky, A. R. *Adv. Heterocycl. Chem.* **1984**, *36*, 1-173.
37. Günther, H. *NMR-Spektroskopie*, 3rd ed.; Thieme: Stuttgart, 1992; p 79.
38. An example involving vicinal CN groups: Acherki, H.; Alvarez-Ibarra, C.; Alfonso-de-Dios; Quiroga, M. L. *Tetrahedron* **2002**, *58*, 3217-3227.
[http://dx.doi.org/10.1016/S0040-4020\(02\)00234-X](http://dx.doi.org/10.1016/S0040-4020(02)00234-X)
39. Ohkura, K.; Sugaoi, T.; Ishihara, T.; Seki, K. *Heterocycles* **2004**, *64*, 57-60.
[http://dx.doi.org/10.3987/COM-04-S\(P\)36](http://dx.doi.org/10.3987/COM-04-S(P)36)
40. Yoshimi, Y.; Konishi, S.; Maeda, H.; Mizuno, K. *Synthesis* **2001**, 1197-1202.
<http://dx.doi.org/10.1055/s-2001-15068>
41. Staubach, B.; Buddrus, J. *Angew. Chem.* **1996**, *108*, 1443-1445.
<http://dx.doi.org/10.1002/ange.19961081222>;
Staubach, B.; Buddrus, J. *Angew. Chem. Intl. Ed.* **1996**, *35*, 1344-1346.
<http://dx.doi.org/10.1002/anie.199613441>
42. Wernerova, M.; Hudlicky, T. *Synlett* **2010**, 2701-2707.
<http://dx.doi.org/10.1055/s-0030-1259018>
43. Mauser, H.; Gauglitz, G. *Photokinetics – Theoretical Fundamentals and Applications (Comprehensive Chemical Kinetics*, ed. by R. G. Crampton, G. Hancock), Elsevier: Amsterdam, 1998; Vol. 36, Ch. 4, Sect. 4.2.6.1, pp 263-267.
44. Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252-258.
<http://dx.doi.org/10.1021/ar00080a004>
45. Van Wolven, C.; Döpp, D.; Henkel, G. *Z. Naturforsch. B.* **2006**, *61b*, 301-310.
<http://znaturforsch.com/ab/v61b/s61b0301.pdf>
46. Balasubramanian, K. K.; Selvaraj, S. *J. Org. Chem.* **1980**, *45*, 3726-3727.
<http://dx.doi.org/10.1021/jo01306a040>
47. Derdour, A.; Benabdallah, T.; Marah, B.; Texier, F. *Bull. Soc. Chim. Fr.* **1990**, 69-78.