View Online / Journal Homepage / Table of Contents for this issue

Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 7599

www.rsc.org/obc

EMERGING AREA

The photo-dehydro-Diels–Alder (PDDA) reaction

Pablo Wessig,* Annika Matthes and Charlotte Pick

Received 2nd July 2011, Accepted 9th August 2011
DOI: 10.1039/c1ob06066j

The photo-dehydro-Diels–Alder (PDDA) reaction is a valuable extension of the classical Diels–Alder (DA) reaction. The PDDA reaction differs from the DA reaction by the replacement of one of the C–C-double bonds of the diene moiety by a C–C triple bond and by the photochemical triggering of the reaction. This entails that, in contrast to the DA reaction, the PDDA reaction proceeds according to a multistage mechanism with biradicals and cycloallenes as intermediates. The PDDA reaction provides access to a considerable variety of compound classes. For example, 1-phenylnaphthlenes, 1,1′-binaphthyls, *N*-heterocyclic biaryls, and naphthalenophanes could be obtained by this reaction.

Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

1. Introduction

Cyclic molecular structures are widely disseminated both in natural products and synthetic compounds and therefore the development of new cyclization methods is an important task of preparative organic chemistry. Among the vast variety of cyclization reactions, cycloadditions occupy a special place because two or more bonds of the formed ring are established simultaneously. One of the most efficient of these reactions is the Diels–Alder (DA) reaction[1] which is the [4 + 2] cycloaddition between a diene and an alkene or alkyne (also called the dienophile, Fig. 1a). One or more of the six carbon atoms involved in the DA reaction can be replaced by heteroatoms (oxygen or nitrogen) and the term hetero Diels–Alder (HDA) reaction[2] is used for this variant. The DA products have in common that unsaturated but not aromatic rings are formed (unless the newly formed double bond is part of an aromatic system, *e.g.* DA reactions of *o*-quinodimethanes[3]). If one of the double bonds of the diene component is replaced by a triple bond, the reaction is now called dehydro-Diels–Alder (DDA) reaction,[4] which has profound effects on the outcome of the DA reaction. In contrast to the classical DA reaction cyclic allenes are the primary products, which are usually not stable but rearrange (*cf.* section 2). If the dienophile is also an alkyne, this rearrangement leads to a new aromatic ring (Fig. 1b).

In fact the construction of new aromatic rings is a characteristic feature of the DDA reaction. As the first example of a DDA reaction Michael and Bucher[5] reported in 1895 on the

Institut für Chemie, Universität Potsdam, Karl-Liebknecht Str. 24–25, D-14476, Potsdam, Germany

Pablo Wessig

Pablo Wessig was born in Görlitz in 1962, completed his Ph.D. graduation at the Humboldt-University of Berlin in 1990. After a postdoctoral stay at the University Basel, Switzerland, in the group of B. Giese (1993) he attended the habilitation in 2000. In 2008 he was appointed as Professor for Bioorganic Chemistry at the University of Potsdam. His primary research interests are focused on preparative organic photochemistry, molecular probes and rigid molecular sticks.

Annika Matthes

Annika Matthes was born in Berlin in 1980, started to study chemistry in 2000 and finished with her diploma degree in 2006. She is now working on her PhD in the group of Prof. Pablo Wessig.

Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

dimerization of 3-phenylpropiolic acid upon prolonged heating in acetic anhydride. A few years later Pfeiffer and Möller[6] described a similar reaction of ethyl 3-phenylpropiolate under drastic conditions (200 °C, sealed tube). In the subsequent seven decades a limited number of synthetic applications has been published.[7] Considerable improvement concerning the reaction conditions could also be achieved by transition-metal catalysis.[8]

Already in 1948 Baddar and co-workers mentioned rather casually their observation concerning the DDA reaction of phenylpropiolic anhydride: *"This conversion was effected by either* (*a*) *heating phenylpropiolic anhydride on the water-bath for 15–20 mins., or* (*b*) *exposing its benzene solution* (*trace of iodine*) *to sunlight for several days."* [7e]

This barely noticed result can be considered as the birth of the photo-dehydro-Diels–Alder (PDDA) reaction (although this term has not been used in the literature until much later) which is the subject of this review. The synthesis of the PDDA reactants is normally not outlined in this review and we refer to the cited literature.

2. Mechanism of the PDDA reaction

The chief subject of this review is the preparative scope of the PDDA reaction and therefore the reaction mechanism will only be briefly discussed. A detailed discussion of the mechanism is to be found in some of our previous publications.[9,10] It should be mentioned that the current state of knowledge concerning the PDDA mechanism is mainly based on DFT calculations.

Whereas the DA reaction proceeds in a concerted manner in most cases and no intermediates are formed, the PDDA reaction (and presumably also the DDA reaction) is a stepwise process. As described in section 3, in most of the hitherto known PDDA applications the diene component is an arylalkyne and we therefore discuss the mechanism for this case. (It cannot be completely ruled out that the reaction proceeds slightly different if enynes are used instead of arylalkynes, see section 3).

The basics of the PDDA reaction mechanism are summarized in Scheme 1. The reaction commences with a photochemical excitation of the arylalkyne **1**. Although the residue R^1 can be an alkyl group[11] it has proved to be beneficial if R^1 is an acyl group (ketone or ester), because the excitation wavelength is long-

Charlotte Pick

Charlotte Pick, born in Bad Soden/a. Ts. in 1977, obtained her chemistry diploma in the group of Prof. U. Koert at the Philipps University in Marburg. In 2005 she joined the group of Prof. P. Wessig to work towards her PhD degree. Her research focuses on the PDDA reaction and its asymmetric variant and application to pyridyl derivatives.

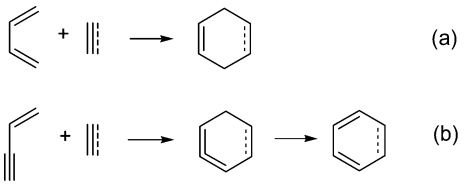
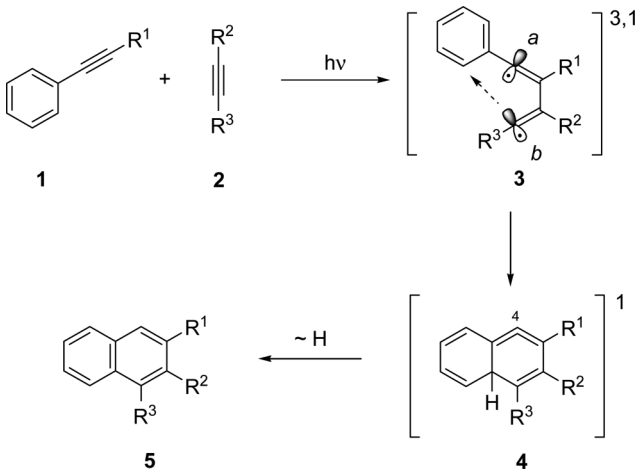


Fig. 1 Diels–Alder (a) *vs.* dehydro-Diels–Alder (b) reaction.



Scheme 1 Mechanism of the PDDA reaction.

wave shifted. The DFT calculations and sensitization/quenching experiments[9,10] indicate that an intersystem crossing (ISC) to the triplet state is mandatory for the initial step of the reaction, which is the formation of a C–C single bond between the alkyne moieties providing the 1,3-butadiene-1,4-diyl biradicals **3** (*a*, *b* denote the radical centers). It should be mentioned that this step has considerable similarities to the initial step of the Bergman cyclization.[12] In this case too, photochemical variants have been published.[13] At the stage of biradicals **3** the ISC back to the singlet state presumably takes place. In the next step the radical center *b* (Scheme 1) attacks an *ortho* position of the aromatic ring to give the highly strained cyclic allene **4**. It is important to note that an alternative attack of radical center *a* may occur if R^3 is also an aromatic ring. To understand the next step it is important to realize that the electronic structure of **4** is dominated by a zwitterionic rather than a biradical configuration with a distinct negative partial charge at C-4. Therefore the hydrogen migration in the final step is in fact a proton migration (mostly mediated by the solvent) rather than a migration of a hydrogen atom.

3. PDDA applications

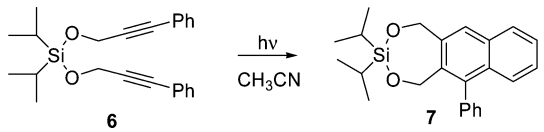
3.1. 1-Phenylnaphthalenes

In 1995, Bradford, Fleming and Ward reported on the photochemical cyclization of silylether **6** to the 1-phenylnaphthalene **7**, unfortunately without stating a yield.[11] An analogous intermolecular reaction of 3-phenylpropyn-1-ol (the reactant for the preparation of **6**) is not known and therefore it is obvious that the linking of phenylalkyne moieties is mandatory for this type

 This journal is © The Royal Society of Chemistry 2011

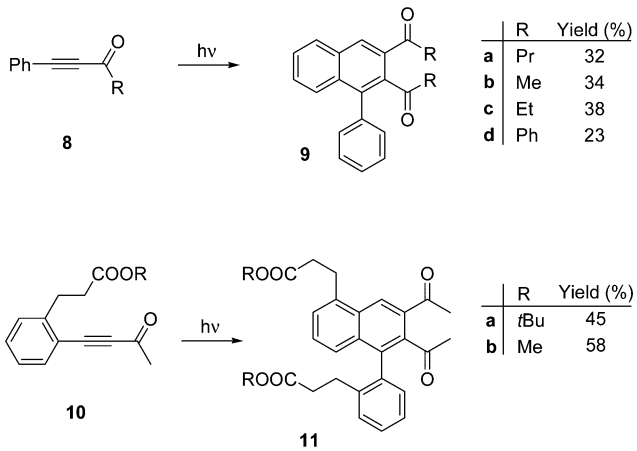
Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

of PDDA reaction. It should be noted that the cyclization of **6** required irradiation with short-wave UV light in quartz vessels (Scheme 2).



Scheme 2 PDDA cyclization of silylether **6**.

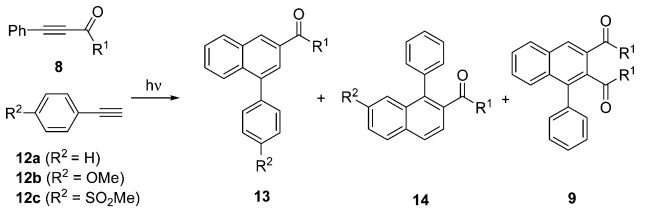
Excited reactants such as **6** presumably feature a low ISC rate to the triplet state and therefore react from the excited singlet state. The short lifetimes of these states explain the low reactivity in intermolecular reactions. Instead, 3-arylynones efficiently populate a long-lived triplet state and smoothly undergo an intermolecular PDDA reaction. For example, various 3-phenylynones **8** and *ortho*-substituted 3-phenylynones **10** were dimerized to the corresponding naphthalene derivatives **9** and **11**, respectively (Scheme 3).[14]



Scheme 3 Intermolecular PDDA of ynones **8** and **10**.

If ynones **8** are irradiated in the presence of phenylethyne (**12a**) or 4-substituted derivatives (**12b,c**) compounds **13** and **14** are obtained as a result of an intermolecular cross-PDDA. Only in two cases (entries 1 and 3) the dimerization products **9** were formed as byproducts. Furthermore, the regioselectivity of the ring closure in favour of **13** is remarkable. It could be explained by the higher reactivity of the upper radical center of the 1,3-butadiene-1,4-diyl intermediate (*cf*. Scheme 1). This hypothesis is supported by the outcome of the reaction between **8** and **12b** (entry 4). The methoxy group as an electron donor diminishes the mentioned radical reactivity and facilitates the formation of **14** (Scheme 4).[14]

Although Schemes 3 and 4 demonstrate that the *intermolecular* PDDA reaction is versatile, the yields are rather moderate in most cases. A distinct improvement is achieved, if the two reactive components of the PDDA reaction are connected with a linker. The first collection of reactants bearing such a linker has in common the presence of one or two keto groups adjacent to the alkyne moiety. Different structural variations were investigated to explore the synthetic scope of the PDDA reaction. The diketones **15a–c** were investigated to find out the influence of the chain length *n* on the PDDA reaction. Here a length of *n* = 3 (entry 2) is obviously optimal whereas shorter or longer chains afforded the



Entry		R^1	R^2	Solvent	13	14	9
1	**a**	Me	H	*t*BuOH	32%	4%	20% (**9b**)
2	**a**	Me	H	MeOH	30%	7%	0% (**9b**)
3	**b**	Pr	H	*t*BuOH	39%	0%	6% (**9a**)
4	**c**	Me	OMe	MeOH	21%	12%	0% (**9b**)
5	**d**	Me	SO_2Me	MeOH	35%	0%	0% (**9b**)

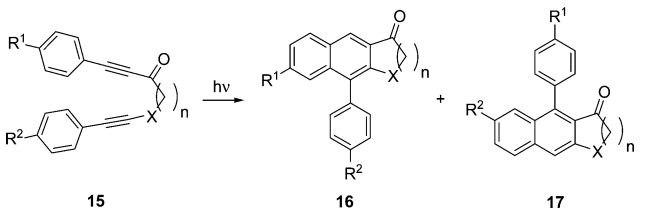
Scheme 4 Intermolecular cross-PDDA reaction.

Table 1 Yields of PDDA products **16** and **17**

Entry	No.	X	*n*	R^1	R^2	**16** [%][a]	**17** [%][a]
1	**a**	CO	2	H	H	30	—[b]
2	**b**	CO	3	H	H	54	—[b]
3	**c**	CO	4	H	H	32	—[b]
4	**d**	CH_2	2	H	H	36	51
5	**e**	CH_2	1	H	H	24	50
6	**f**	CH_2	1	H	OMe	30	57
7	**g**	CH_2	1	OMe	H	32	55
8	**h**	CH_2	1	H	Cl	32	22
9	**i**	CH_2	1	Cl	H	13	60
10	**j**	CH_2	1	H	CF_3	43	25
11	**k**	CH_2	1	CF_3	H	8	61

[a] Yields of **16** and **17**. [b] **17** is identical to **16**.

products **16** with lower yields. If one of the keto groups is replaced by a methylene group (**15d–k**), two isomeric products **16** and **17** may be formed, and it was investigated in which way the selectivity of the cyclization could be influenced. Whereas the length of the linker has only marginal influence on the **16**/**17** selectivity (entries 4 and 5) the impact of substituents R^1 and R^2 in 4-position of the aromatic rings was very instructive. The electron donating methoxy group causes only small changes in the **16**/**17** selectivity (entries 6 and 7). On the other hand, electron withdrawing groups such as Cl or CF_3 considerably enhance the selectivity (entries 8–11), whereby the extent of this effect depends on where this group is tethered (Scheme 5, Table 1).[9,14]

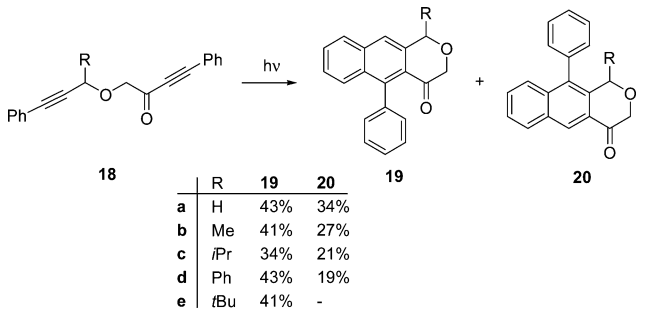


Scheme 5 PDDA cyclization of ketones **15**.

Besides influencing the regioselectivity of the second C–C bonding step (**3**→**4**, *cf*. Scheme 1) by electronic effects, steric hindrance was taken into consideration. For this purpose, the ethers **18a–e** were prepared and the photochemical behavior was evaluated. A look at the yields is very enlightening and reveals a common problem of the PDDA reaction. The bigger the residue R, the lower is the yield of isomer **20** and in the case of a *tert*-butyl group (**18e**) only product **19** is formed. On the other hand, the

Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

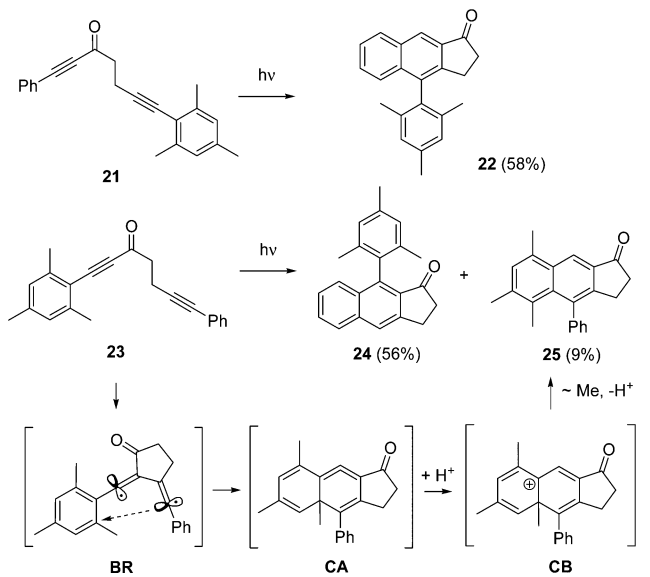
yields of compounds **19** are nearly unaffected (except for **19c**) and do not increase with increasing size of R. This suggests that an unfavorable product is simply decomposed *e.g.* at the stage of the biradical **3** and that the second C–C-bond formation is apparently irreversible (Scheme 6).[10]



	R	19	20
a	H	43%	34%
b	Me	41%	27%
c	*i*Pr	34%	21%
d	Ph	43%	19%
e	*t*Bu	41%	-

Scheme 6 PDDA cyclization of ether ketones **18**.

The third approach to influence regioselectivity of the PDDA ring closure is to block the *ortho* positions which will then not be attacked. This is demonstrated based on mesityl substituted ketones **21** and **23**. In both cases the expected 1-mesitylnaphthalenes **22** and **24** are obtained as main products. Surprisingly, the byproduct **25** was also isolated upon irradiation of **23**. A plausible explanation could be that at the stage of the biradicals **BR** an attack on a methyl substituted *ortho* position takes place, followed by protonation of the resulting cycloallene **CA** to give the highly delocalized carbenium ion **CB**. A final 1,2-methyl migration followed by deprotonation provides compound **25**. This means that substituents with an increased anionotropic migration tendency (*e.g.* alkyl groups) only partially fulfil the function of blocking (Scheme 7).[9]



Scheme 7 Scope and limitation of blocking *ortho* positions in the PDDA reaction.

3.2. 1,1′-Binaphthyls

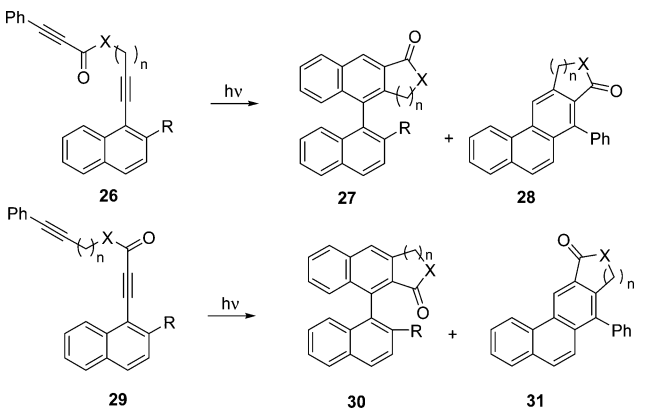
1,1′-Binaphthyls have gained great importance as chiral ligands and auxiliaries.[15] 1,1′-Binaphthyl-2,2′-diol (BINOL)[16] and

Table 2 Yields of products **27**, **28** and **30**, **31**

Reactant	*n*	R	X	Products
26a	1	H	O	**27a** (38%), **28a** (41%)
26b	1	OMe	O	**27b** (46%)
26c	2	H	O	**27c** (41%), **28b** (30%)
26d	2	OMe	O	**27d** (38%)
26e	2	H	CH_2	**27e** (13%), **28c** (17%)
29a	1	OMe	O	**30a** (36%)
29b	2	H	O	**30b** (26%), **31a** (23%)
29c	2	OMe	O	**30c** (28%)
29d	1	OMe	CH_2	**30d** (18%)

2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)[17] should be mentioned as particularly prominent examples.

The preparation of 1,1′-binaphthyls by the PDDA reaction requires the presence of a 1-naphthyl moiety in the reactant structure. For this purpose the photochemical behavior of a series of mono- and disubstituted napthalenes **26** and **29** was investigated. Here too, blocking of the 2-position of the naphthalene moiety is critical for the selective formation of 1,1′-binaphthyls. If this position is unsubstituted (**26a,c,e**, **29b**) the phenanthrenes **28** and **31**, respectively, are obtained in nearly the same amounts as the desired 1,1′-binaphthyls **27** and **30**, respectively. On the other hand, the latter are exclusively obtained if the 2-position is blocked by a methoxy group (**26b,d**, **29a,c,d**, Scheme 8, Table 2).[18]



Scheme 8 Photochemical behavior of naphthalenes **26** and **29**.

In all of the hitherto discussed systems (except **6**) an ynone group has functioned as the chromophoric group. As mentioned in section 2, this group ensures an efficient formation of the triplet state by a rapid ISC. This does not apply to esters **26a–d** and **29a–c** and, consequently, these compounds show a low photochemical reactivity if irradiated in solvents commonly used for the PDDA reaction (*e.g.* alcohols, benzene). The problem can be solved by the use of acetone as solvent, which acts as an efficient triplet sensitizer. It should be noted that the irradiation of esters under these conditions afforded the PDDA products with considerably higher yields than the ketones **26e** and **29d**.[18]

The potential application of 1,1′-binaphthyls as chiral reagents or catalysts inspires investigations towards asymmetric variants of the PDDA reaction. Using the experiences gained with compounds **26** and **29**, the photochemical behavior of esters **32** in acetone as a triplet sensitizer was investigated. The hope was that a chirality center in the reactant (identified by an asterisk in the formula of **32**) more or less efficiently induces the chirality

 This journal is © The Royal Society of Chemistry 2011

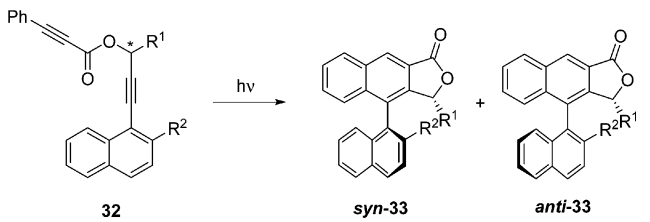
View Online

Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

Table 3 Yields of 1,1′-binaphthyls **33**

	R^1	R^2	Yield **33** [%]	*syn* : *anti*
a	*t*Bu	OMe	86	50 : 50
b	Ph	OMe	36	43 : 57
c	4-CF_3–Ph	OMe	75	58 : 42
d	Mes	OMe	47	**38 : 62**
e	Ph	COOMe	28	52 : 48
f	Mes	COOMe	70	57 : 43

of the newly formed chirality axis. Unfortunately, the observed stereoselectivities are low and a *syn* : *anti* ratio of 1 : 2 was obtained in the best case (Scheme 9, Table 3).[19]



32 ***syn*-33** ***anti*-33**

Scheme 9 Asymmetric PDDA reaction of compounds 32.

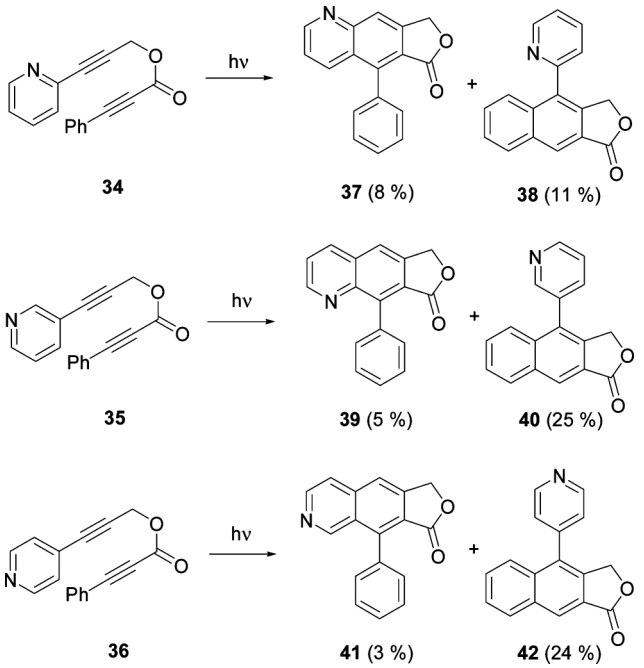
3.3. *N*-Heterocyclic biaryls

N-Heterocyclic biaryls are widely used as mono- and bidentate ligands for the complexation of various metal cations, especially those of transition metals.[20] As a prominent example 2,2′-bipyridyl should be mentioned. To investigate whether the PDDA reaction is extensible on pyridines instead of carbocyclic aromatic rings, the isomeric 3-pyridylpropargyl esters **34–36** were prepared and irradiated. Due to the concurrence of the pyridyl and the phenyl moiety at the stage of the 1,3-butadiene-1,4-diyl biradicals both phenylquinolines or -isoquinolines (**37**, **39**, **41**) and naphthylpyridines (**38**, **40**, **42**) were expected as products. Unfortunately, these two reaction channels were nearly equally pursued with a slight preference of the naphthylpyridines (Scheme 10).[21]

To suppress the undesired attack on the 3-position of the pyridine ring in **34**, blocking of this position with a methoxy group (**43**) proved to be useful. Irradiation of **43** provided the naphthylpyridine **44** with 34% yield. Changing the position of the ester carbonyl group (**45**), however, gave rise to a distinct decrease of the yield of naphthylpyridine **46** (Scheme 11).[21]

3.4. Naphthalenophanes

Cyclophanes are molecules consisting of an aromatic unit (*e.g.* benzene, naphthalene) and a chain (which may contain further aromatic units) forming a bridge between two non-adjacent positions of the aromatic unit. If the aromatic unit is a naphthalene moiety these compounds are called naphthalenophanes,[22] and the linked positions are prefixed in parentheses, *e.g.* (1,5)naphthalenophanes.[23] In the preceding sections it was demonstrated that the PDDA reaction allows a flexible access to highly substituted naphthalenes and it should, therefore, be possible to prepare naphthalenophanes by this method. These compounds are a promising synthetic target due to their potentially high ring strain and their axial chirality. Very recently, this approach

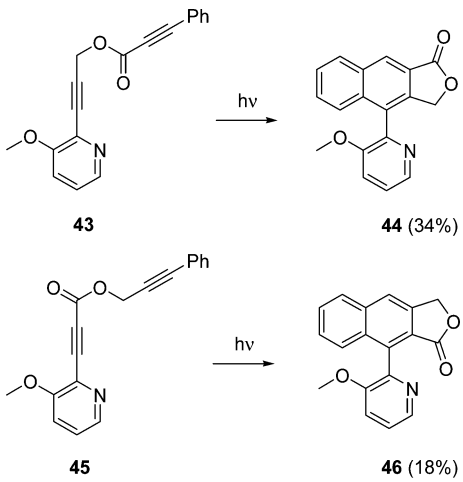


34 **37** (8 %) **38** (11 %)

35 **39** (5 %) **40** (25 %)

36 **41** (3 %) **42** (24 %)

Scheme 10 Photochemical behavior of 3-pyridylpropargyl esters **34–36**.

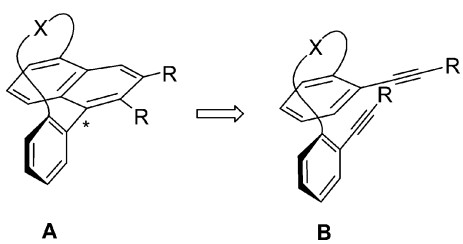


43 **44** (34%)

45 **46** (18%)

Scheme 11 Irradiation of compounds **43** and **46**.

was successfully substantiated with the preparation of a series of (1,5)naphthalenophanes **A** by PDDA cyclization of *ortho*-substituted bis(arylalkynes) **B** where the *ortho* positions are joined by a chain **X** (Scheme 12).[24]



A **B**

Scheme 12 Retrosynthetic approach to (1,5)naphthalenophanes **A**.

The variation of the chain **X** was accomplished with the aim of exploring the scope of the macrocyclization with respect to ring

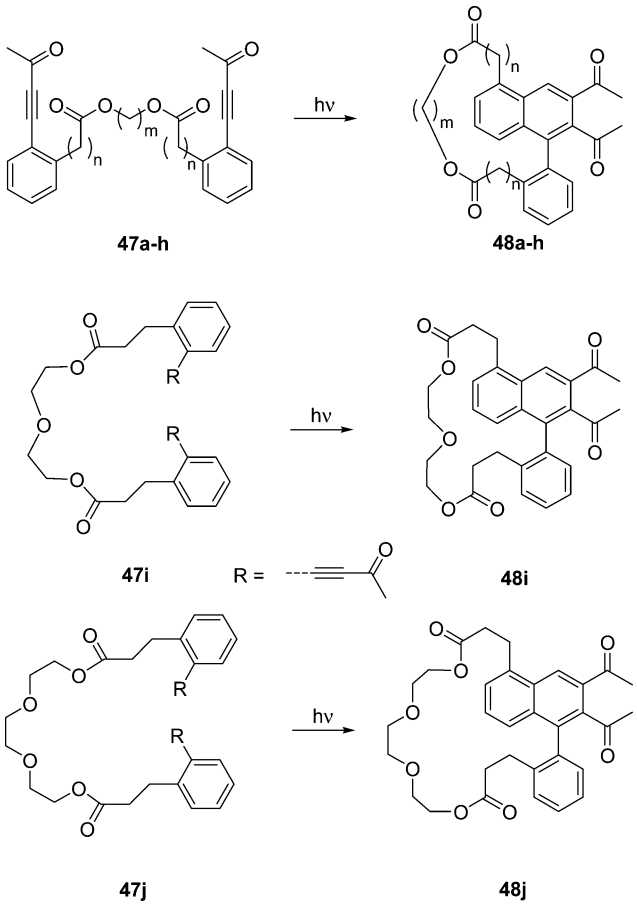
Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012

Table 4 Yields of naphthalenophanes **48**

	n	*m*	*N*[a]	Yield [%]
a	0	2	6	6
b	1	2	8	15
c	0	4	8	16
d	1	4	10	48
e	2	2	10	37
f	2	4	12	38
g	2	5	13	29
h	2	6	14	30
i	—[b]	—[b]	13	41
j	—[b]	—[b]	16	50

[a] N = 2*n* + *m* + 4. [b] see Scheme 13.

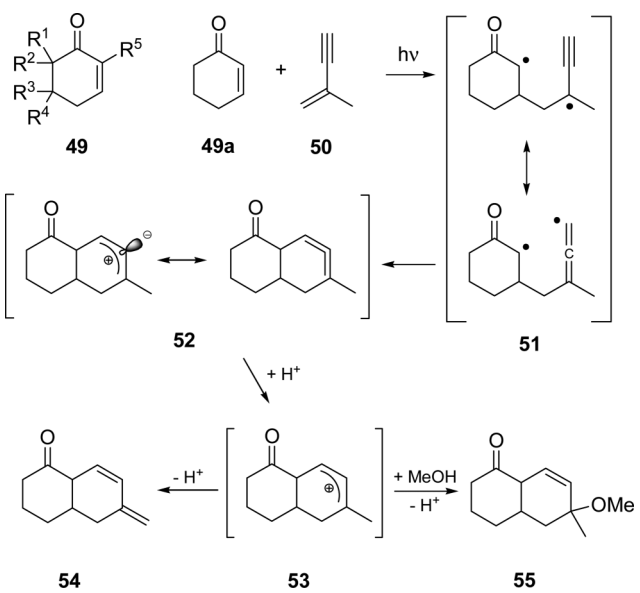
strain and size. A modular structure based on diesters of three different carboxylic acids with various diols enabled a variation of the chain length *N* between 6 and 16 atoms. Naphthalenophanes **48a–c** with a short chain length (*N* = 6, 8) were obtained only in low yields (Table 4), which can be explained by the considerable ring strain of these compounds due to deformation of the naphthalene moiety and chain **X** (**48a**: 31.0 kcal mol^{-1}, **48b**: 7.1 kcal mol^{-1}, **48c**: 11.8 kcal mol^{-1}, based on DFT-calculations).[24] Another strain phenomenon is observed with medium sized rings and is attributable to unfavorable nonbonding interactions. This is responsible for the moderate yields of **48g,h**. In all other cases the naphthalenophanes were obtained with satisfactory yields. It should be noted that (1,5)naphthalenophanes **48** are axially chiral and the enantiomers could be separated by chiral HPLC. Furthermore, the absolute configuration of the enantiomers was determined by CD-spectroscopy (Scheme 13).[24]



Scheme 13 Preparation of (1,5)naphthalenophanes **48**.

3.5. PDDA reaction of cyclohexenones

Another type of intermolecular PDDA reaction was discovered by Margaretha in connection with the comprehensive investigations of the photochemistry of cyclic enones **49**.[25] For the sake of clarity, the mechanism of this reaction is explained in Scheme 14 by the reaction of the parent compound cyclohexenone **49a** and 2-methyl-1-buten-3-yne **50**. In contrast to most of the PDDA reactions discussed so far, it is not the enyne moiety, but rather the enone that is electronically excited. In the initial step, the biradical **51** is formed by a C–C-bond formation between the β-position of enone and enyne. The second, non-photochemical step affords the cycloallene. As pointed out several times in this article, cycloallenes are best described as zwitterionic in terms of electronic configuration rather than by a biradical one with a considerable basicity at the central carbon atom of the allene. Consequently, cycloallene **52** is easily protonated to the allylcation **53**, which either eliminates to diene **54** or undergoes addition of methanol giving ether **55**.



Scheme 14 Intermolecular PDDA reaction of cyclohexenones.

4. Summary

This review article demonstrates the preparative versatility of the photo-dehydro-Diels–Alder (PDDA) reaction as a valuable extension of the classical Diels–Alder (DA) reaction and the dehydro-Diels–Alder (DDA) reaction. The photochemical activation of the reactants and the associated large amount of energy enables the synthesis of molecules, which are often not accessible by a DA or DDA approach. The synthetic scope ranges from phenylnaphthalenes (section 3.1.), 1,1′-binaphthyls (section 3.2.), *N*-heterocyclic analogues of phenylnaphthalenes (section 3.3.) through to in part highly strained naphthalenophanes (section

 This journal is © The Royal Society of Chemistry 2011

3.4.). In the first half of section 3.5. it is shown that the PDDA reaction of butenynyl arenes is a powerful benzoannelation method whereas the second half of this section describes the PDDA reaction between excited cyclohexenones and 2-methyl-1-buten-3-yne. In view of the variety of the presented examples it can be expected that further interesting applications of the PDDA reaction will be developed in the future.

References

1 (*a*) J. A. Norton, *Chem. Rev.*, 1942, **31**, 319; (*b*) J. G. Martin and R. K. Hill, *Chem. Rev.*, 1961, **61**, 537; (*c*) G. Brieger and J. N. Bennett, *Chem. Rev.*, 1980, **80**, 63; (*d*) H. B. Kagan and O. Riant, *Chem. Rev.*, 1992, **92**, 1007; (*e*) J. D. Winkler, *Chem. Rev.*, 1996, **96**, 167; (*f*) A. Kumar, *Chem. Rev.*, 2001, **101**, 1; (*g*) K.-i. Takao, R. Munakata and K.-i. Tadano, *Chem. Rev.*, 2005, **105**, 4779.

2 (*a*) S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, 1962, **62**, 405; (*b*) D. L. Boger, *Chem. Rev.*, 1986, **86**, 781.

3 (*a*) W. Oppolzer, *Synthesis*, 1978, 793; (*b*) J. L. Charlton and M. M. Alauddin, *Tetrahedron*, 1987, **43**, 2873; (*c*) J. L. Charlton, *Can. J. Chem.*, 1986, **64**, 720; (*d*) K. C. Nicolaou, D. Gray and J. Tae, *Angew. Chem., Int. Ed.*, 2001, **40**, 3675.

4 P. Wessig and G. Müller, *Chem. Rev.*, 2008, **108**, 2051.

5 A. Michael and J. E. Bucher, *Ber. Dtsch. Chem. Ges.*, 1895, **28**, 2511.

6 P. Pfeiffer and W. Möller, *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 3839.

7 (*a*) J. E. Bucher, *J. Am. Chem. Soc.*, 1910, **32**, 212; (*b*) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1935, 636; (*c*) R. D. Haworth and W. Kelly, *J. Chem. Soc.*, 1936, 745; (*d*) F. G. Baddar, *J. Chem. Soc.*, 1947, 224; (*e*) F. G. Baddar and L. S. El-Assal, *J. Chem. Soc.*, 1948, 1267; (*f*) F. G. Baddar and L. S. El-Assal, *J. Chem. Soc.*, 1951, 1844; (*g*) F. G. Baddar, L. S. El-Assal and N. A. Doss, *J. Chem. Soc.*, 1959, 1027; (*h*) D. Brown and R. Stevenson, *J. Org. Chem.*, 1965, **30**, 1759; (*i*) L. H. Klemm, K. W. Gopinath, D. H. Lee, F. W. Kelley, E. Trod and T. M. McGuire, *Tetrahedron*, 1966, **22**, 1797; (*j*) F. G. Baddar, G. E. M. Moussa and M. T. Omar, *J. Chem. Soc. C*, 1968, 110.

8 (*a*) E. Müller, M. Sauerbier, D. Streichfuß, R. Thomas, W. Winter and G. Zountsas, *Justus Liebigs Ann. Chem.*, 1971, **750**, 63; (*b*) E. Müller and G. Odenigbo, *Justus Liebigs Ann. Chem.*, 1975, 1435; (*c*) F. Wagner and H. Meier, *Tetrahedron*, 1974, **30**, 773.

9 P. Wessig, G. Müller, A. Kühn, R. Herre, H. Blumenthal and S. Troelenberg, *Synthesis*, 2005, 1445.

10 P. Wessig, G. Müller, R. Herre and A. Kühn, *Helv. Chim. Acta*, 2006, **89**, 2694.

11 C. L. Bradford, S. A. Fleming and S. C. Ward, *Tetrahedron Lett.*, 1995, **36**, 4189.

12 (*a*) R. G. Bergman, *J. Am. Chem. Soc.*, 1972, **94**, 660; (*b*) R. G. Bergman, *Acc. Chem. Res.*, 1973, **6**, 25; (*c*) T. P. Lockhart and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 4091; (*d*) W.-M. Dai, *Curr. Med. Chem.*, 2003, **10**, 2265; (*e*) M. Kar and A. Basak, *Chem. Rev.*, 2007, **107**, 2861.

13 (*a*) N. J. Turro, A. Enenzahav and K. C. Nicolaou, *Tetrahedron Lett.*, 1994, **35**, 8089; (*b*) A. Enenzahav and N. J. Turro, *J. Am. Chem. Soc.*, 1998, **120**, 1835; (*c*) G. B. Jones and K. C. Russell, in: W. Horspool and F. Lenci (ed.)*CRC Handbook of Organic Photochemistry and Photobiology* (2nd Ed.), CRC-Press, Boca Raton 2004, pp. 29/1–29/21; (*d*) D. Falcone, J. Li, A. Kale and G. B. Jones, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 934.

14 P. Wessig, G. Müller, C. Pick and A. Matthes, *Synthesis*, 2007, 464.

15 (*a*) P. Kocovsky, S. Vyskocil and M. Smrcina, *Chem. Rev.*, 2003, **103**, 3213; (*b*) R. Noyori, *Adv. Synth. Catal.*, 2003, **345**, 15.

16 J. M. Brunel, *Chem. Rev.*, 2005, **105**, 857; J. M. Brunel, *Chem. Rev.*, 2005, **105**, 4233.

17 R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345.

18 P. Wessig and G. Müller, *Chem. Commun.*, 2006, 4524.

19 P. Wessig and G. Müller, *Aust. J. Chem.*, 2008, **61**, 569.

20 J. R. Gispert, *Coordination Chemistry*, Wiley, New York, 2008.

21 P. Wessig and C. Pick, *J. Photochem. Photobiol. A: Chem.*, 2011, **222**, 263.

22 F. Vögtle, R. Schäfer, L. Schunder and P. Neumann, *Justus Liebigs Ann. Chem.*, 1970, **734**, 102.

23 F. Vögtle and P. Neumann, *Tetrahedron Lett.*, 1969, **10**, 5329.

24 P. Wessig and A. Matthes, *J. Am. Chem. Soc.*, 2011, **133**, 2642.

25 (*a*) B. Witte and P. Margaretha, *J. Inf. Rec.*, 2000, **25**, 225; (*b*) B. Witte, L. Meyer and P. Margaretha, *Helv. Chim. Acta*, 2000, **83**, 554.

Published on 10 August 2011 on http://pubs.rsc.org | doi:10.1039/C1OB06066J
Downloaded by Universitaire d'Angers on 12 February 2012