Light induced cycloadditions of captodative alkenes

D DÖPP*, J BREDEHORN, A W ERIAN†, A JUNG,
H LANFERMANN, H R MEMARIAN§, B MÜHLBACHER
and M PIES

Fachgebiet Organische Chemie, Universität–GH–Duisburg, D-47048 Duisburg, Germany

†Present address: Department of Chemistry, Cairo University, Giza, Cairo, Egypt

§Present address: Department of Chemistry, University of Esfahan, Esfahan 81744, Iran

Abstract. Triplet excited 1-acylnaphthalenes add captodative alkenes, especially 2-aminoacrylonitriles, in a formal [4 + 2] mode to form 1,4-dihydro-1,4-ethanonaphthalenes. This reaction is in some cases preceded by an independent and ultimately less efficient photoreversible 1,2-addition yielding cyclobutanaphthalene derivatives. There is no indication of a common intermediate partitioning into both types of products. Both additions occur with remarkable regio- and stereoselectivity. The chirally labelled alkene *S* or *R*-2-(2-methoxymethyl-1-pyrrolidinyl)acrylonitrile is added in the [4 + 2] mode with over 99% diastereoselectivity leading to practically enantiomerically pure 1,4-adducts. Sensitized cycloadditions of 2-morpholinoacrylonitrile are also discussed briefly.

Keywords. Photocycloadditions; triplet excited state; 1,4-dihydro-1,4-ethanonaphthalenes; tetrahydrocyclobuta[*a*]naphthalenes; asymmetric induction.

1. Introduction

Photocycloadditions of alkenes to aromatic nuclei continue to be of considerable interest (McCullough 1987). In recent years, numerous novel [4 + 2] cycloadditions of so called captodative (Viehe *et al* 1985) alkenes to carbon atoms 1 and 4 of 1-acylnaphthalenes have been observed (Döpp *et al* 1985, 1989; Döpp and Memarian 1986, 1990; Memarian 1986; Pies 1989; Mühlbacher 1991). Most recently, novel 1,8-photoadditions of alkenes in a formal [3 + 2] mode to naphthalene 1,4-dicarboxylates and 1,4-dicarbonitriles have been reported (Kubo *et al* 1992).

The 1,4-additions to acylnaphthalenes observed by us are of marked regio-, stereo- and diastereoselectivities and are occasionally preceded and/or accompanied by 1,2-additions. Our findings, including hitherto unpublished work, will be summarized and interpreted in the following sections.

2. Results

2.1 1,4-Ethanonaphthalenes and tetrahydrocyclo-buta[*a*]naphthalenes from 1-naphthyl carbonyl compounds

Triplet-excited 1-acetonaphthone (**1b**) as well as photoexcited 1-naphthaldehyde (**1a**) and 1-naphthophenone (**1c**) form 1,4-photoadducts of type 4 with various

*For correspondence

2-aminoacrylonitriles (**2**) in a highly regio- and stereoselective manner (Döpp *et al* 1985; Pies 1989; Döpp and Memarian 1990; Mühlbacher 1991). Without exception, only the benzenoid ring bearing the acyl group is affected. Most investigations have been carried out using 1-acetonaphthone (**1b**) as substrate. Rate constants for quenching of triplet-**1b** by various type **2** alkenes range from 3×10^8 to 3×10^9 $\text{M}^{-1}\text{s}^{-1}$ in methanol or acetonitrile and are thus smaller than the diffusion controlled limit (Döpp *et al* 1990).

When we repeated our earlier preparative runs, we found that besides the donor-*syn* products **4a-i** ($\text{R} = \text{COCH}_3$ in most cases), minor amounts of the donor-*anti* adducts **5a-h** are formed, the *syn/anti* ratio varying between 95:5 and 89:11 (Mühlbacher 1991).

The same trend is observed when methyl-1-naphthoate (**1d**) is photoexcited in the presence of type **2** olefins (*syn/anti* varying from 95:5 to 88:12). Thus, the aromatic ester **1d** exhibits photochemical behaviour parallel to that of the aromatic ketone **1b** (Mühlbacher 1991).

Such regio- and stereoselective 1,4-additions to acynaphthalenes are not restricted to 2-aminoacrylonitriles. Very similar results are obtained with 2-(*tert*-butylthio)acrylonitrile (Döpp *et al* 1989). A remarkably high (>99%) double diastereofacial differentiation leading to practically enantiomerically pure adducts (+)– or (–)–**4k** can be demonstrated in the [4+2]-photoaddition of either (*S*)- or (*R*)-(2-methoxymethyl-pyrrolidin-1-yl)acrylonitrile (**2k**) to 1-acetonaphthone (**1b**) (Döpp and Pies 1987). The absolute configuration of (+)–**4k** and (–)–**4k** (as shown) has been derived from a comparison of ^1H -NMR-chemical shifts of (+)–**4k** with those of analogous 1,4-adducts, in which the donor-*syn* geometry had clearly been demonstrated by either X-ray structural analysis (Döpp *et al* 1985, 1989) and/or NOE intensity difference determinations (Mühlbacher 1991), together with the determination of the circular dichroism in the hydrogenated ketone (+)–**7** (Pies 1989). From the positive sign for the Cotton-effect in its n, π^* -absorption the absolute arrangement of the benzenoid ring (formally representing a double bond) and the oxo-group at C-9 (Legrand and Rougier 1977) as depicted is clearly established. Since both the ketones (–)–**6** and (+)–**6** had been demonstrated to be practically free of the respective enantiomers by HPLC using a chiral stationary phase (Döpp and Pies

1987), (*S*) – 2k is added solely with its re-face to the si-face of 1b, and (*R*) – 2k solely with its si-face to re-1b.

The origin of the high differentiation observed with 2k must be sought in the properties of the donor auxiliary and its capabilities for complexation either within a pre-oriented complex of the reactants or within a preferred conformation of a favourable precursor diradical collapsing to 4k.

Although temperature-dependency studies, which could cast some light on the relative importance of the precursors mentioned, have not been made yet (and probably will be difficult due to the thermal lability of products of type 4), two levels of selection may be envisaged as outlined in recent pioneering work on the temperature-dependence of asymmetric induction in the Paterno–Büchi reaction (Buschmann *et al* 1989).

It had been observed earlier (Memarian 1986; Pies 1989), that 2a and 2g also give rise to minor amounts of type 3 adducts of hitherto not clarified configuration at C-2. It could be shown unambiguously that 2i definitely adds to photoexcited 1b to form 3i prior to the appearance of 4i in the photolysis mixture. Upon prolonged irradiation, however, 3i is degraded again due to its styrene-like and therefore (compared to 4i) conjugated chromophore into starting materials, from which relatively photostable 4i is finally formed. Further, since by X-ray single-crystal structure determination the configuration of 3i has recently been established to be rel-(2*S*, 2*aS*), that is with the hexamethyleneimino group *anti* to the dihydronaphthalene moiety, a direct interconversion of 3i into 4i with least motion of the groups involved is not possible but would require a 180° torsion around the former cyclobutanaphthalene C-1/C-2 bond.

1,2- and 1,4-Additions selectively to the benzenoid nucleus are observed when common solutions of 2g and methyl 8-quinoline carboxylate (8) are irradiated

(>280 nm) in benzene or acetonitrile solution (Döpp and Jung 1992). Again, it can be demonstrated that products **9** and **10** emanate from parallel reactions, and that after long irradiation times, **10** is favoured at the expense of **9**.

From this, and the aforementioned case, it may be ruled out that a common intermediate, e.g. the diradical **D**, connects type 3 and type 4 products. On the other hand, a diradical like **D** is an attractive and also logical intermediate in the 1,4-addition, since from spectroscopic (Döpp *et al* 1990) and quenching studies (Döpp *et al* 1985; Pies 1989; Mühlbacher 1991), the lowest (π, π^*) excited triplet state is envisaged as the reactive state in the 1,4-cycloadditions observed. Most logically, this state is followed by a triplet diradical obtained from addition of one molecule of olefin.

Quantum yields of product formation do not exceed 0.02, this may reflect low rates of diradical formation and/or efficient fragmentation of unfavourable (extended) conformations of diradicals like **D** into starting materials (Buschmann *et al* 1989). It should be stressed, however, that complex-forming orientation of the reactants prior to or after excitation cannot be ruled out at this stage. Neither a ground-state interaction nor an exciplex following the triplet have been detected experimentally, though.

The unique substitution pattern of captodative (Viehe *et al* 1985) alkenes (one donor and one acceptor group at the same terminus of the double bond) does indeed manifest special features in light-induced cycloadditions. This may also be demonstrated by the comparison of the reactivity of excited 1-acetonaphthone (**1b**) towards acrylonitrile, 2-(*tert*-butylthio)acrylonitrile and *tert*-butyl vinyl sulphide.

Acrylonitrile is not added at all, and, in contrast to the very regio- and stereoselective addition of 2-(*tert*-butylthio)acrylonitrile giving rise solely to product **11**, *tert*-butyl vinyl sulphide is added with complete lack of regio- and stereoselectivity to form a mixture of all four *a priori* possible regio- and stereoisomeric 1,4-dihydro-1,4-ethanonaphthalenes (**12**, **13**) (Döpp and Memarian 1986; Lanfermann

1990). Vinyl ethers, on the other hand, prefer 1,2-addition to **1b,d** (Döpp and Lanfermann 1992), and conventional enamines could not be added in any way to acynaphthalenes.

It had been tempting to compare the reactivity of excited 1-naphthonitrile (**14**) with that of the acynaphthalenes **1a-d** towards a representative captodative alkene. Electronically excited **14**, probably via its first excited singlet state (McCullough 1987), adds **2g** with the same direction of addition as observed with **1a-d** to yield 1,2-adducts **15** and **16**. In the main product **15**, the *syn*-orientation of the morpholino group and 1,2-dihydronaphthalene moiety is again derived from an X-ray single crystal structure determination and from NOE intensity difference studies (Döpp *et al* 1993). Solely NOE results support the *syn* orientation in by-product **16**.

2.2 Morpholinoacrylonitrile cyclodimerizations

Whereas 2-alkylthioacrylonitriles tend to dimerize spontaneously (Gundermann and Röhl 1974), such behaviour is unknown for 2-aminoacrylonitriles.

2-Acetonaphthone and naphthalene-1,8-dicarboxylic acid N-methylimide were found to sensitize, albeit in low yield, the [2 + 2] head-to-head dimerization of

2-morpholinoacrylonitrile (**2g**) (Memarian 1986; Döpp and Bredehorn 1993). The *trans* structure of the dimer **17** has been confirmed by single-crystal X-ray structural analysis. The rôle of the sensitizers is still not quite clear, since the photodimerization of **2g** cannot be driven to yields larger than 12%, whereas the [2 + 2] dimerization of 2-aminoacrylonitrile, sensitized by benzophenone, has been reported to provide a 75% yield of both diastereomeric head-to-head dimers (Ksander *et al* 1987).

In addition, both benzophenone and 2-acetonaphthone cause the formation of another cyclodimer from **2g**, to which structure **18** has been assigned on the basis of its 300 MHz ^1H -NMR-spectrum (Döpp and Bredehorn 1993).

3. Conclusion

The highly regio- and stereoselective photoadditions to the naphthalene skeleton, as described here, had not been expected. They add cycloadditions originating from a triplet-excited state to the already rich cycloaddition photochemistry of aromatic compounds starting from excited singlets. Selectivities observed must be attributed at least partly to the unique substitution pattern of captodative alkenes. Since the aminonitrile function at carbon atoms 9 in products of type **4** and **5** and at carbon 2 in **3** may be hydrolysed to give way to an oxo-group, the photoadditions described practically make novel 1,4-dicarbonyl compounds accessible. Thus captodative alkenes function as ketene equivalents in cycloadditions.

Acknowledgements

The authors are very much indebted to G Henkel, University of Duisburg, for recent unpublished single-crystal X-ray structural determinations and to the late G Snatzke, University of Bochum, for a Cotton-effect determination. Thanks are due to the Deutsche Forschungsgemeinschaft for a fellowship granted to H -R Memarian and to the A V Humboldt-Foundation for a fellowship awarded to Á W Erian. Generous financial support of this work by the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie, is gratefully acknowledged.

References

- Buschmann H, Scharf H -D, Hoffmann N, Plath M W and Runsink J 1989 *J. Am. Chem. Soc.* **111** 5367
 Döpp D and Bredehorn J 1993 (unpublished) (Part of planned doctoral thesis by J Bredehorn, University of Duisburg)

- Döpp D, Erian A W and Henkel G 1993 *Chem. Ber.* **126** 239
- Döpp D and Jung A 1992 (unpublished) (Part of planned doctoral thesis by A Jung, University of Duisburg)
- Döpp D, Krüger C, Memarian H -R and Tsay Y -H 1985 *Angew. Chem., Int. Ed. Engl.* **24** 1048
- Döpp D and Lanfermann H 1992 (unpublished) (Part of planned doctoral thesis by H Lanfermann, University of Duisburg)
- Döpp D and Memarian H -R 1986 *Substituent effects in radical chemistry* (eds) H G Viehe, Z Janousek and R Merenyi (NATO ASI Series, C 189) (Dordrecht: Reidel) p. 383
- Döpp D and Memarian H -R 1990 *Chem. Ber.* **123** 315
- Döpp D, Memarian H -R, Krüger C and Raabe E 1989 *Chem. Ber.* **122** 585
- Döpp D, Memarian H -R, van Eijk A M J and Varma C A G O 1990 *J. Photochem. Photobiol.* **A53** 59
- Döpp D and Pies M 1987 *J. Chem. Soc., Chem. Commun.* 1734
- Gundermann K -D and Röhl E 1974 *Lieb. Ann. Chem.* 1661
- Ksander G, Bold G, Lattmann R, Lehmann C, Früh T, Xiang Y -B, Inomata K, Buser H P, Schreiber J, Zass E and Eschenmoser A 1987 *Helv. Chim. Acta* **70** 1115
- Kubo Y, Inoue T and Sakai H 1992a *J. Am. Chem. Soc.* **114** 7660
- Kubo Y, Noguchi T and Inoue T 1992b *Chem. Lett.* 2027
- Lanfermann H 1990 *Photocycloaddition of tert-butyl vinylsulfide to 1-acetonaphthone*, diploma thesis, University of Duisburg
- Legrand L M and Rougier M J 1977 *Stereochemistry Fundamentals and methods. Vol. 2. Determination of configuration by dipole moments CD or ORD* (ed.) H B Kagan (Stuttgart: Thieme) p.33
- McCullough J J 1987 *Chem. Rev.* **87** 811, and references cited therein
- Memarian H -R 1986 *Photoadditions of captodative olefins to acynaphthalenes*, doctoral thesis, University of Duisburg.
- Mühlbacher B 1991 *Photocycloaddition of captodative olefins to 1-acetonaphthone and methyl 1-naphthoate*, doctoral thesis, University of Duisburg
- Pies M 1989 *Regio-, diastereo- and enantioselectivity in a photo-Diels-Alder-addition*, doctoral thesis, University of Duisburg
- Viehe H -G, Janousek Z, Merényi R and Stella L 1985 *Acc. Chem. Res.* **18** 148, and references cited therein