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Diels–Alder reactions of anthracene, 9-substituted anthracenes and 9,10-disubstituted anthracenes

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1. Introduction

Anthracene was first isolated in 1833 from coal tar. Since its discovery it has been used for a diverse range of chemical applications from the preparation of alizarin dyes to use in electroluminescent devices. As such, much varied and interesting chemistry has been developed for the functionalisation and modification of the anthracene aromatic ring system. However, perhaps one of the more intriguing aspects of the chemistry of anthracene is the ability to undergo both thermal and photochemical Diels–Alder cycloadditions with a variety of dienophiles across the 9 and 10 positions. This report aims to give an overview of such reactions of anthracene, 9-subtituted anthracenes and 9,10-substituted anthracenes.

Keywords: Diels–Alder reaction; dienophile; [4+2] cycloaddition reaction.
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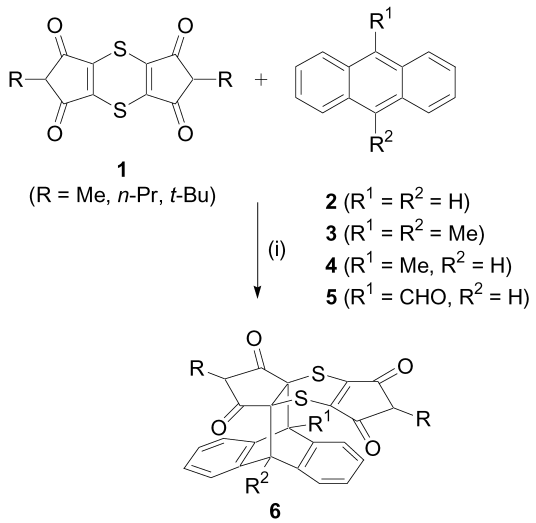
2. Mechanism of Diels–Alder reactions with anthracene

2.1. Thermal mechanism

The mechanism of the thermal [4+2] cycloaddition reaction of anthracene with a dienophile has been the source of much conjecture.[1] The stereochemistry of the reaction involves exclusive *cis* addition of the dienophile to anthracene where the *cis* or *trans* stereochemistry of the dienophile is retained in the product.[2] The retention of stereochemistry has led many groups to postulate a concerted mechanism, where the new σ bonds are formed simultaneously either by direct addition, or via an intermediate charge–transfer complex or an electron donor–acceptor molecular complex.[2] Another possibility is a two-step reaction mechanism where the reaction proceeds via a zwitterionic or diradical intermediate.[2] For a two-step mechanism to occur with retention of stereochemistry, the second step of the reaction would have to be much faster than the rotation about the C–C σ bond of the intermediate formed in the first step.

Many studies have noted the production of a transient colour that disappears as the thermal Diels–Alder reaction proceeds. This has been attributed to the formation of a charge–transfer complex during the course of the reaction and seems, therefore, to provide evidence for a concerted mechanism.[1,3,4] Studies carried out with 1,4-dithiins **1** and anthracene **2** and its derivatives **3**–**5** (Scheme 1) have shown that the formation of the Diels–Alder adducts **6** can in fact occur either via a charge–transfer complex or by direct addition, depending on the properties of the anthracene derivative used.[5]



Scheme 1. *Reagents and conditions*: (i) C_6H_6, △.

The first pathway proceeding via the formation of a charge–transfer complex was dominant when using anthracene **2** and the electron-rich derivatives **3** and **4**. Evidence for charge–transfer complex formation came from the colour change seen during the course of the reaction. The formation, and subsequent disappearance of the charge–transfer complex was monitored using UV spectrophotometry observing absorption bands in the region of 400 to 650 nm. The second pathway, by direct cycloaddition, was only available for the modestly electron-deficient anthracene derivative **5**. The change in mechanism was accompanied by a decrease in the reaction rate. In terms of FMO theory, the rate trend paralleled the HOMO energy levels with charge–transfer complex formation only occurring when the HOMO–LUMO energy difference between diene and dienophile was small, whereas the direct cycloaddition mechanism occurred when this difference was much larger.

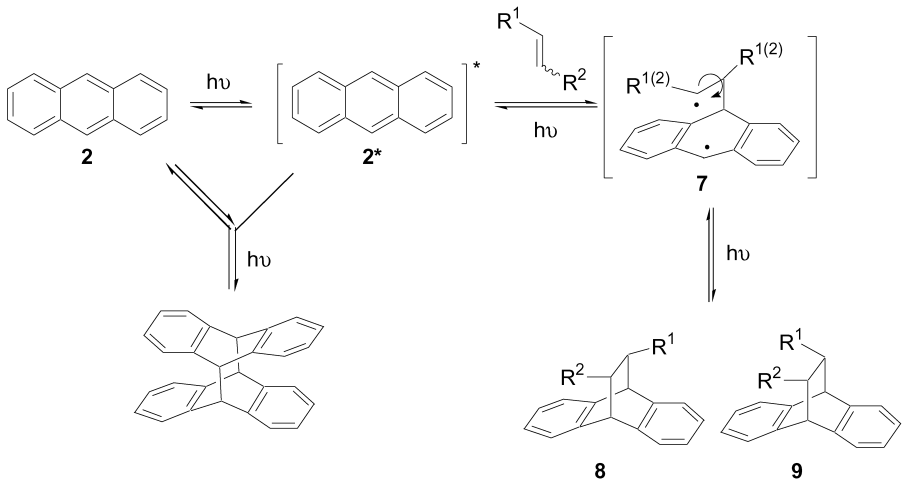
The effect of solvent on the rate of reaction has been studied by many groups.[2,3,6–8] The electron-donating ability of the solvent has been shown to be an important factor that affects the rate of reaction. Electron-donating solvents increase solvation of the dienophile that can in turn decrease the reaction rate.[9] Solvents that are electron accepting can, in some cases, increase the rate of reaction by stabilisation of the transition state, which can be regarded as being electron rich.[8,9] Aromatic solvents produce large increases in reactivity with dienophiles that are capable of very strong charge–transfer interactions,[6] while salt effects have been observed for reactions performed in water.[10,11] However, in general, the influence of the solvent on the rate of reaction, independent of the system investigated, has been shown to be relatively small, rarely above a factor of ten. This can be seen as evidence for a concerted mechanism as solvent effects would be expected to be large if a stepwise mechanism was in operation due to solvent stabilisation/destabilisation of zwitterionic or diradical intermediates.[3,6] However, the use of highly-fluorinated solvents has been shown to have a dramatic effect on the rate of the Diels–Alder reaction of 9-hydroxymethylanthracene and *N*-ethylmaleimide.[12] Additionally, changes in the solvent can also have an effect on the *endo*/*exo* selectivity of the Diels–Alder reaction by a complex combination of solvent solvophobicity, dipolarity and hydrogen bond-donating effects.[8]

The rate of the Diels–Alder reaction of anthracene appears to be governed much more by temperature and substituent effects.[3,13–15] As the Diels–Alder reaction of anthracene is an equilibrium process, changes in temperature have a decisive effect on the position of the equilibrium. Lower reaction temperatures coupled with an excess of dienophile can increase the forward reaction rate, whereas higher temperatures can actually favour the retro Diels–Alder reaction. This has been clearly demonstrated in studies where the amounts of adduct obtained from the reaction of a diene (D) and maleic anhydride (M) using different reaction conditions were measured and compared (Table 1).[16]

Table 1. Effect of reaction conditions upon the equilibrium position of the Diels–Alder reaction

Diene	Adduct in equilibrium mixture (%)		
	1:1 (D:M) in xylene	1:30 (D:M) in xylene	1:1 (D:M) in benzene
Anthracene	99	–	–
9-Methylanthracene	99	–	–
9,10-Dimethylanthracene	98	–	–
9-Phenylanthracene	75	97	–
9,10-Diphenylanthracene	16	78	–
1,2-Benzanthracene	84	99	–
1,2,5,6-Dibenzanthracene	30	91	–
3-Methylcholanthrene	22	83	94

Substituent effects have been found to be much more complex, with either substituents on anthracene, substituents on the dienophile, or a combination of the two features to be considered. In general, the reactivity of anthracene can be increased by substitution with electron-donating groups in the 9 and 10 positions, whereas electron-withdrawing substituents have the opposite effect.[3,16,17] However, in some cases, the steric effect of substituents can decrease the reaction rate by overriding any electronic effects. For example, substitution with the normally-electron-donating Me_3Si group in the 9 position results in very little rate enhancement over anthracene, and disubstitution with Me_3Si leads to a complete lack of reactivity.[3] The relationship between electronic and steric effects has been shown to be complex, with sterically-demanding groups often reacting faster than less bulky groups. It has been suggested that this effect is due to a



Scheme 2.

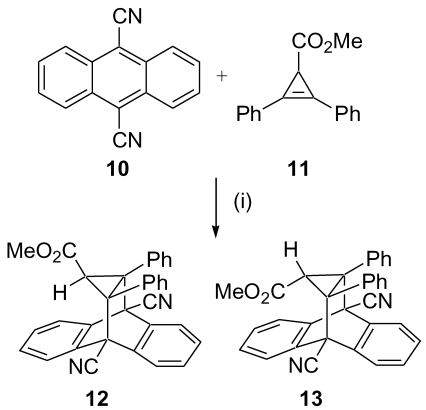
release of the compression placed on bulky groups by the *peri* hydrogen atoms of anthracene with the change in hybridisation from sp^2 to sp^3 that occurs in the Diels–Alder reaction.[3]

The dienophile in the Diels–Alder reaction may be considered to have Lewis acid character, accepting the π electrons from a donor (the diene).[13,18] The main effect of substituents on the dienophile is to alter the electronic properties, thus changing its ability to accept π electrons.[14,15,17] Therefore, electron-withdrawing substituents generally increase the reactivity of the dienophile by increasing its ability to accept π electrons. Again, the relationship between steric and electronic effects is complex, but substituents that can hinder attack from either side of the plane of the dienophile generally have a detrimental effect on the rate of reaction. For example, the reactivity of α-substituted maleic anhydride derivatives was shown to be reduced when highly-branched substituents (e.g. isopropyl and cyclopentyl) were used.[13] This was thought to be due to the low number of conformations that the substituent could adopt where attack from either side of the plane of the dienophile was possible. When less-highly-branched substituents were used, the number of conformations that the substituent could adopt was thought to be much greater. Certainly, the detrimental effect on the reactivity was either much less pronounced or non-existent.

2.2. Photochemical mechanism

The unimolecular photochemical dimerisation of anthracene has a long history that has been extensively reviewed.[19–22] In brief, Fritzsche discovered in 1866 that solar irradiation of a saturated benzenic solution of a hydrocarbon, later named 'photene', led to a crystalline compound, later named 'paraphotene', which reverted back to the starting material thermally. Later, photene was identified as anthracene and paraphotene was shown to be a dimer that, unlike anthracene, did not emit fluorescence. Subsequently, the structural properties of 9-substituted anthracene photodimers were investigated. Two monomers of 9-substituted anthracene were found to associate with a head-to-head or a head-to-tail manner leading to head-to-head and head-to-tail photodimers.

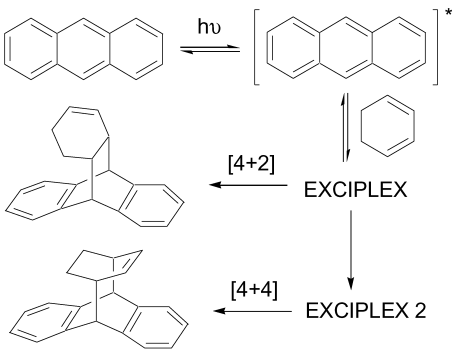
Whereas the Woodward–Hoffmann rules dictate that [4+4] concerted photocycloadditions, like those above, are allowed processes, [4+2], concerted photocycloadditions are symmetry forbidden reactions.[23,24] Therefore, the photocycloaddition of a dienophile to anthracene would be expected to occur via a symmetry-allowed stepwise process. An extensive study into the photochemical Diels–Alder reactions of anthracene **2** revealed that high-frequency UV light results in photoinduced electron transfer to produce anthracene in a singlet state form $\mathbf{2}^*$.[25,26] This quickly reacted via a diradical mechanism with a variety of electron-deficient dienophiles to give the adducts **8** and **9** (Scheme 2). The formation of the intermediate **7** allows rotation around the C–C bond, leading to the selective formation of the more stable *trans*-adduct **8**. The reaction was monitored using the fluorescent properties of the singlet state form. If no electron-deficient dienophile was present, then the singlet state anthracene dimerised. The reverse reaction, producing the starting materials, was performed using high-frequency UV light. Further studies showed that, in non-polar solvents, singlet-excited 9,10-dicyanoanthracene **10** and 1,2-diphenylcyclopropene-3-carboxylate **11** form a photochemical charge–transfer complex or exciplex which yielded the *exo* Diels–Alder adduct **12** (Scheme 3).[27] In polar solvents, however, no exciplex emission was observed and the isomeric *endo* adduct **13** was produced, along with the dimer of **11** (no dimerisation of **10** was noted).



Scheme 3. *Reagents and conditions*: (i) $h\nu^*$, solvent (*405, 436 nm).

Formation of the less-sterically-favoured *endo* adduct was thought to be due to epimerisation of the radical cation of the dienophile produced during the reaction in polar solvents. Interestingly, the adduct **12** was found to decompose to its components thermally, whereas the adduct **13** showed no such decomposition.

Studies into solvent effects on exciplex formation, carried out with anthracene and 9-cyanoanthracene, found that reactions with conjugated dienophiles gave increased quantities of [4+4] adducts in polar solvents via a concerted pathway, with decreased production of the [4+2] adducts from a stepwise pathway.[28] The reactions with 9-cyanoanthracene were found to produce even higher yields of the [4+4] adducts than those with anthracene. A possible explanation for the results obtained was that after an exciplex had been formed via the interaction of anthracene in its singlet excited state and the ground state conjugated dienophile (EXCIPLEX, Scheme 4), either a stepwise reaction could occur to give the [4+2] adduct, or a concerted reaction via another unspecified intermediate complex (EXCIPLEX 2, Scheme 4) to give the [4+4] adduct. It was thought that this second intermediate complex was stabilised more by polar solvents than the first exciplex and that this resulted in the increase in the [4+4] reaction noted in polar solvents. The reaction of 9-cyanoanthracene would produce more polar exciplex complexes and therefore a higher stabilisation of the second intermediate complex in polar solvents would be expected to occur, leading to a greater increase in the production of the [4+4] adducts.



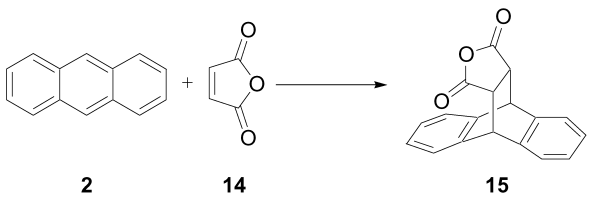
Scheme 4.

3. Thermal Diels–Alder reactions

3.1. Additions to anthracene

The types of dienophile used in the Diels–Alder reactions of anthracene fall broadly into four classes, namely (i) α,β-unsaturated carbonyls, (ii) alkenes attached to a heteroatom or halogen, (iii) alkenes and alkynes and (iv) heterodienophiles. The first reported cycloaddition of a dienophile, in this case maleic anhydride **14**, to anthracene **2** via a fusion reaction at 260°C was by Diels and Alder in 1931 (Scheme 5).[29] Subsequently, Clar obtained the same adduct **15** by heating a solution of the two reactants in xylenes.[30]

The thermal reaction of anthracene with various maleic anhydride-type dienophiles (e.g. substituted maleic



Scheme 5.

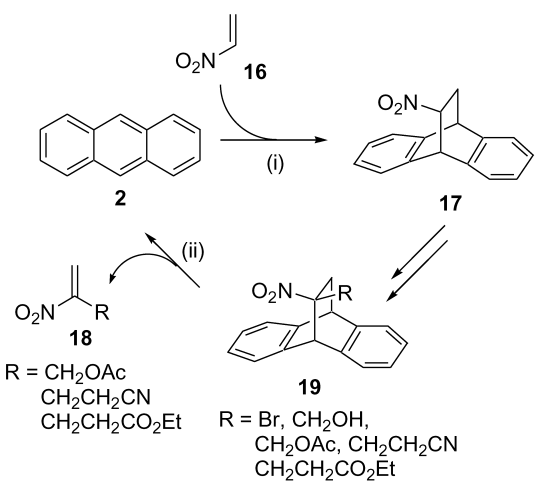
anhydrides and *N*-substituted maleimides) has since become one of the most well-studied reactions of anthracene.[18,31–39] As a general method, reflux in a suitable solvent (e.g. benzene, toluene, etc) has been the most applicable for these reactions. Some of the reactions of anthracene with various dienophiles performed in this way are summarised in Table 2.

Table 2. Thermal Diels–Alder reactions of anthracene with various dienophiles

Dienophile	Solvent	Time	Yield (%)[a]
Maleic anhydride[31]	Dioxane	2 h	67
Maleic anhydride[34]	*p*-Xylene	10 min	90
p-Benzoquinone[40]	Xylene	2 h	83
Indanone[41]	Toluene	48 h	68
2-Cyanovinyl ketones[42]	Benzene	43 h	70
Fumaric acid[43]	Dioxane	3 d	82
Dimethyl fumarate[34]	*p*-Xylene	4 h	67
Benzoylacrylic acid[44]	Toluene	2 h	70

[a] The results given are examples and are by no means comprehensive. Many more examples exist in the literature.[15,30–33,38,44–50]

Since the 1980s, interest in the use of microwave-assisted reactions as a clean and more efficient method to effect the cycloaddition reactions of anthracene has grown. The Diels–Alder addition reactions of anthracene with maleic anhydride and dimethyl fumarate have achieved yields of 92 and 87%, with vastly-reduced reaction times of 3 and 10 min, respectively.[34] These reactions were carried out in sealed tubes packed in vermiculite that absorbed the microwave energy and heated the reactions efficiently. These techniques have now been simplified by the use of open systems[35,51] and 'dry' reaction media[36,37,39,51] without loss of yield or increased reaction times. Although the use of

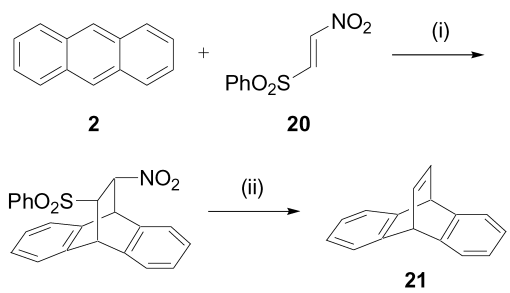


Scheme 6. *Reagents and conditions*: (i) *o*-dichlorobenzene, reflux, 45 min; (ii) △.

this methodology has been limited to relatively simple systems, the potential to expand the scope of the Diels–Alder reaction by the use of microwave irradiation is promising.

The first thermal cycloaddition reactions of anthracene with alkenes were carried out with 1-nitroolefins.[52–55] Using an excess of nitroethylene **16** in refluxing *o*-dichlorobenzene for 45 min gave the adduct **17** in 71% yield and this was used in the preparation of new more-highly-substituted nitroolefins **18** after thermal decomposition of the modified adducts **19** (Scheme 6).[53] The reaction of anthracene with 1-nitronaphthalene at 300°C for 10–15 h followed by aromatisation via loss of nitrous acid has also been reported,[54] and the yields of these reactions were found to be strongly affected by polymerisation of the nitroolefins.[55] Subsequent catalytic hydrogenation or reduction was used to produce the corresponding amines in this study.

β-Sulphonylnitroolefins such as **20** (Scheme 7) have been used as alkene and alkyne equivalents in Diels–Alder reactions with anthracene **2** to overcome the inherent lack of reactivity of unsubstituted alkenes and alkynes in this type of reaction. The high reactivity of the nitro and sulphonyl groups enabled the use of relatively mild conditions for these reactions e.g. toluene, 110°C, 3 h (90% yield) (Scheme 7).[56] Subsequent reductive elimination using Bu_3SnH and AIBN at 80°C gave the cyclic 1,4-diene **21** in high yield (60%).[56,57]

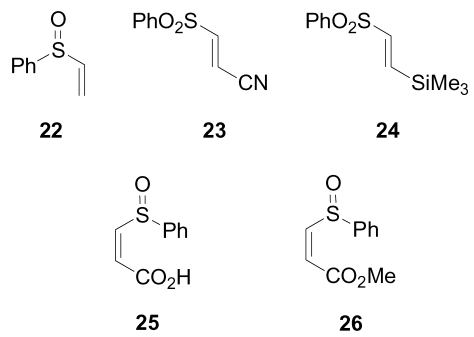


2 20 21

Scheme 7. *Reagents and conditions*: (i) C_6H_5Me, △, 3 h; (ii) Bu_3SnH, AIBN, 80°C, 2 h.

The Diels–Alder addition reactions of β-sulphonylnitroolefins with anthracene have also been used in the preparation of pyrroles fused with polycyclic skeletons.[58] In similar work, phenyl vinyl sulphoxide **22**,[59,60] (*E*)-3-phenylsulphonylprop-2-enenitrile **23**,[61] *trans*-1-benzenesulphonyl-2-(trimethylsilyl)ethylene **24**,[60,62] (*Z*)-3-phenylsulphinylprop-2-enoic acid **25** and its methyl ester **26** (Fig. 1)[63] have been used as synthons for ethylene, cyanoacetylene, 1-alkenes, acetylene and monosubstituted alkynes, respectively, and employed in the construction of functionalised six-membered rings via thermal cycloaddition reactions with anthracene.

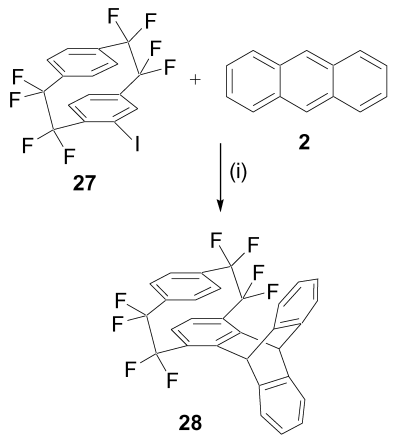
Other thermal Diels–Alder reactions of anthracene with alkenes attached to a heteroatom or halogen include those with tetrachloroethylene,[64] 1,3-diacetylimidazolin-2-one,[65] alkenylimmonium salts,[66] vinyl- and propenyl-phosphines and ethyndiylbis(diphenylphosphine oxide) either by heating at reflux in a solvent or by heating in a sealed tube.[67]



22 23 24 25 26

Figure 1.

Cycloaddition reactions of anthracene have been performed with unfunctionalised alkenes including C_{60},[68,69] $C_{60}F_{18}$[70] and triphenylenetrisendoxides.[71] Although the reaction with triphenylenetrisendoxides only required reflux in xylene for 48 h to give modest yields of the adducts, the reaction with C_{60} required heating the reactants under vacuum in a sealed tube at 200°C for 2 d to give 42% yield of the addition product. Cycloaddition of anthracene **2** with the highly-reactive aryne intermediate generated by deiodination of the cyclophane **27** gave the addition product **28** in excellent yield (84%) (Scheme 8).[72,73]

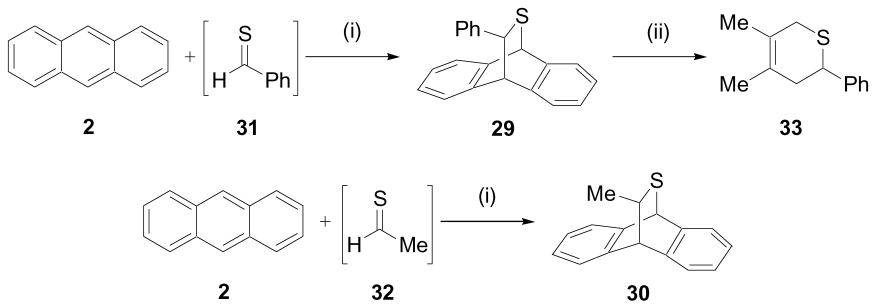


27 2 28

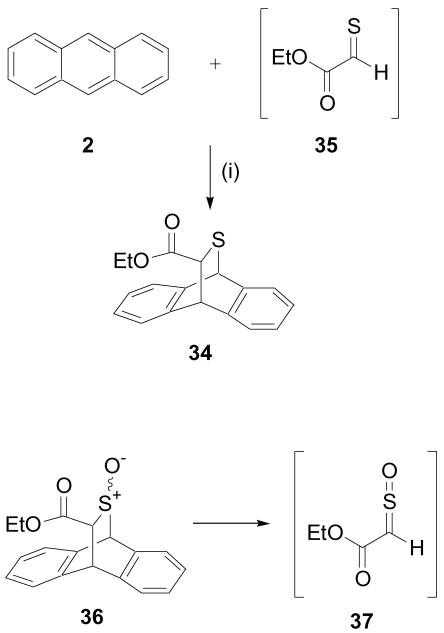
Scheme 8. *Reagents and conditions*: (i) *t*-BuOK, *t*-butylbenzene, △.

The hetero Diels–Alder reaction of anthracene has been used to 'trap' unstable transient compounds as stable cycloadducts. Subsequent release of the reactive intermediate has then been carried out in a controlled manner using retro Diels–Alder methodology. This was effectively demonstrated when the cycloadducts **29** and **30** were obtained in high yields (97 and 82%, respectively) by reaction with the thioaldehydes **31** and **32**, which were produced in situ by thermolysis of the corresponding thiosulphinates (Scheme 9).[74] In the case of the cycloadduct **29**, the thermal retro Diels–Alder/exchange reaction in the presence of 2,3-dimethylbutadiene was then used to produce the dihydrothiopyran **33** in 92% yield.

Similarly, the cycloadduct **34** was obtained in 37% yield by the [4+2] cycloaddition of the transient thioaldehyde ethyl thioxoacetate **35**, produced in situ by the reaction of the sulphenyl chloride with triethylamine (Scheme 10).[75] The cycloadduct was then found to dissociate in refluxing



Scheme 9. *Reagents and conditions*: (i) C_6H_5Me, 97–100°C; (ii) 2,3-dimethylbutadiene, C_6H_5Me, 98–99°C.



Scheme 10. *Reagents and conditions*: (i) $CHCl_3$, △.

toluene, releasing the thioaldehyde for further reaction. Subsequently, reaction of the cycloadduct **34** with 3-chloroperbenzoic acid in CH_2Cl_2 gave the corresponding sulphoxide **36** (Scheme 10).[76] No observations were noted on the level of diastereoselectivity obtained in this reaction. The retro Diels–Alder reaction of the sulphoxide **36** gave the highly-reactive thioaldehyde *S*-oxide **37**.

More recently, the hetero Diels–Alder reaction of anthracene and ethyl 3-oxo-2-thioxobutanoate has been described, along with the transformations of the cycloadduct produced and the subsequent retro Diels–Alder reactions to generate α-imino thioketone *S*-oxides such as **38** (Fig. 2) that were found to be useful in the preparation of sulphur-containing heterocyclic systems.[77]

Nitrogenous dienophiles have also been used successfully in a number of applications. Chiral imines have been

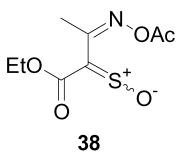


Figure 2.

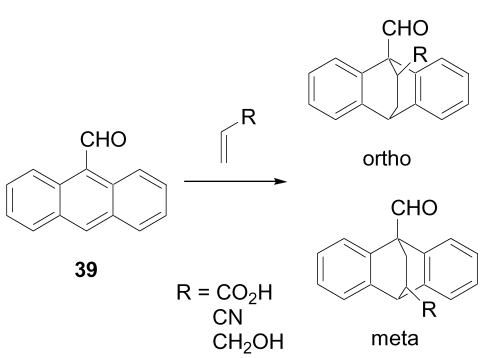
employed in aza-Diels–Alder reactions with anthracene to give a sterically-constrained amino acid derivative in a rather low overall yield,[78] while triazolinedinones have been used to prepare 1,2-diazeines in good yield.[79]

Anthracene has been employed as a protecting group in the synthesis of natural products and natural product fragments as the thermal Diels–Alder reactions with compounds such as benzoquinone,[80,81] *N*-methyl maleimide[33] and methyl acrylate[82] effectively protect the alkene unit from further reaction. Pyrolysis or photochemical methods have been used to effect the retro Diels–Alder reaction once the synthesis is complete.[83–90] This methodology has been applied to the synthesis of molecules such as γ-alkylidene-$\Delta^{\alpha,\beta}$-butenolides,[80] 3-pyrrolines,[33] γ-spirolactones and γ-spirolactams,[82] 3-*O*-demethylfortamine,[81] the monoacetetonide of conduritol A and conduramines[91] and naturally-occurring α-methylenebis-γ-butyrolactones.[92]

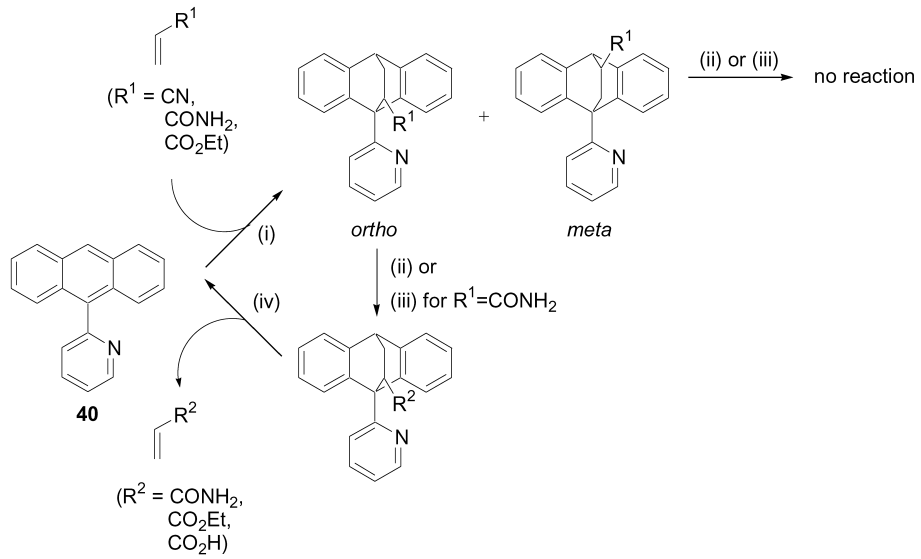
3.2. Additions to 9-substituted anthracene

Since the very first thermal Diels–Alder reaction of 9-substituted anthracene, there has been significant interest in the regioselectivity of these reactions. One of the first investigations in this area involved the thermal cycloaddition reactions of 9-anthraldehyde **39** with maleic anhydride, acrylic acid, acrylonitrile and allyl alcohol to assess its reactivity and selectivity with these dienophiles.[93] The *ortho* products were found to be favoured in all cases (except, of course, maleic anhydride) and the yields obtained ranged between 59 and 78% (Scheme 11).

Subsequent work investigating the regioselectivity of the thermal cycloaddition reactions of some 9-substituted anthracene derivatives has also found that the reactions



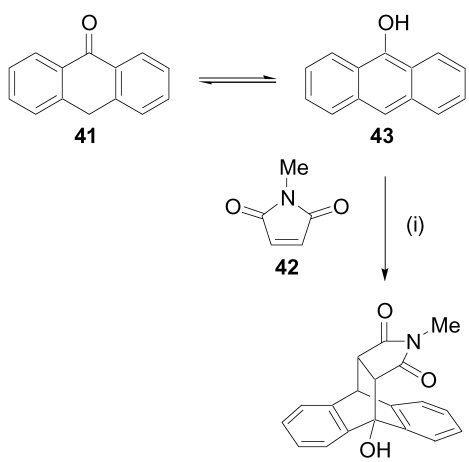
Scheme 11.



Scheme 12. *Reagents and conditions*: (i) △; (ii) $NiCl_2$, dioxane/H_2O; (iii) $NiCl_2$, EtOH; (iv) △.

proceeded to give predominately the *ortho* regioisomer in all but two cases tested (acrylic acid with 9-nitro- and 9-carboxyanthracene).[94] It was found that these ratios remained constant over the course of the reaction, suggesting the products to be of kinetic origin. The preferential formation of the *ortho* isomer in these studies is in agreement with theoretical observations concerning increased molecular orbital overlap with substituted dienes and dienophiles, and experimental observations for the Diels–Alder reactions of other substituted dienes and dienophiles.[95–98]

Interestingly, the selectivity of the thermal cycloaddition reaction was found to be dependent upon the dienophile used when a pyridyl group occupied the 9-position **40**.[99,100] The reaction of acrylonitrile (R^1=CN, Scheme 12) produced a 5.4:1 mixture of the *ortho* and *meta* adducts, whereas the reactions with acrylamide (R^1=$CONH_2$) and ethyl acrylate (R^1=CO_2Et) produced 1:1.6 and 1:1.1 mixtures of the *ortho* and *meta* adducts, respectively. The pyridyl group was also found to act as a ligand for the nickel-catalysed hydration (R^1=CN to R^2=$CONH_2$), alcoholysis (R^1=$CONH_2$ to R^2=CO_2Et) and hydrolysis (R^1=CO_2Et to R^2=CO_2H) of the three dienophiles used.

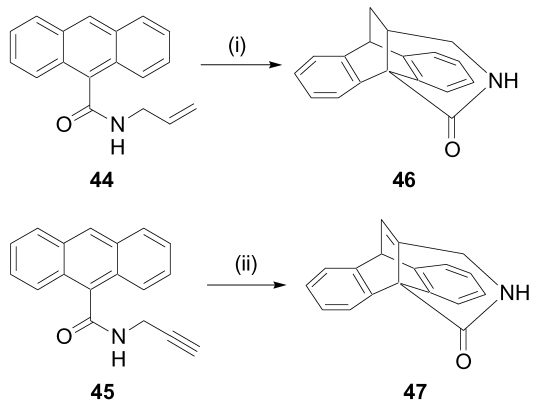


Scheme 13. *Reagents and conditions*: (i) cat. Et_3N.

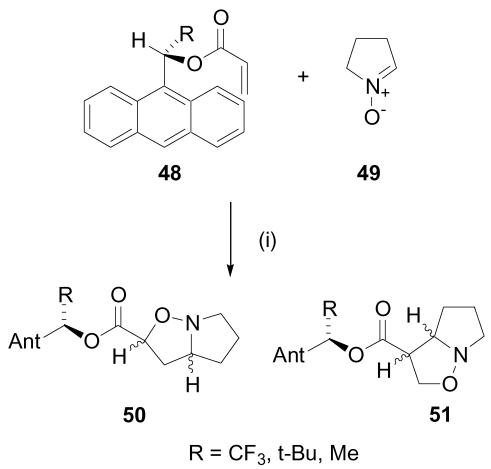
In a slightly different approach to the use of simple thermal conditions, the base-catalysed Diels–Alder reaction of anthrone **41** with *N*-methyl maleimide **42** was studied in an attempt to increase the rate of the reaction.[101] It was noted that the tautomerisation of anthrone to anthracenol **43** was strongly solvent dependent, and that anthracenol was the reactive component in these reactions. The Diels–Alder reactions of anthrone in dimethylformamide, pyridine and triethylamine were found to be complete within a few minutes, whereas the reaction in CH_2Cl_2 was much slower. Subsequently, the reactions using a catalytic amount of triethylamine and employing the dienophile as the solvent were found to give enhanced rates (Scheme 13). Under similar conditions, but using THF as the solvent, dimethyl fumarate, fumaronitrile, maleonitrile and 2-butenolide were found to react, giving the addition products in quantitative yields, but with varying and, in some cases, much longer reaction times.[102] Dimethyl maleate and methyl acrylate were found to be unreactive under these conditions. Further work demonstrated that synergistic reaction conditions employing both an amine base and a Lewis acid led to increased reaction rates for methyl crotonate.[103] Catalytic quantities of a perfluoroalkylated cinchona alkaloid have been used as a chiral base to effect enantioselective variants of this reaction in ≤40% ee.[104]

Biocatalysis has also been used to effect Diels–Alder reactions. 9-Hydroxymethylanthracene was used to covalently link this unit to a ribosome that was employed in Diels–Alder reactions with maleimide derivatives.[105,106] The ribosome was found to accelerate the reaction, but this was limited by the length of the alkyl chain on the maleimide (the optimum length being C_5). It was subsequently found unnecessary to covalently bind the ribosome to the anthracene.

The thermal Diels–Alder reactions of 9-substituted anthracene derivatives with alkenes and alkynes have again been



Scheme 14. *Reagents and conditions*: (i) *p*-xylene, △, 5 h; (ii) *p*-xylene, △, 14 h.



Scheme 15. *Reagents and conditions*: (i) CH_2Cl_2, rt.

studied to a much lesser extent, although more so than with the parent compound. The intramolecular Diels–Alder cycloadditions of the 'tethered' alkenes **44** and alkynes **45** to yield a wide variety of 9,12-bridged ethano- **46** and ethenoanthracenes **47** has been performed at temperatures ranging from 25 to 220°C (Scheme 14).[107] A range of adducts having 3-, 4- and 5-membered bridges, many incorporating heteroatoms, were synthesised. It was found that the ease of cyclisation decreased with increasing bridge length, but neither the diene nor the dienophile needed activating groups to be attached.

The reactions of 9-substituted anthracene derivatives with *trans*-dichloroethene were carried out, in order to investigate the silver-assisted acetolyses and dehydrochlorination of the products.[108,109] The reactants were heated in benzene in a sealed tube at 200°C for 24 h, giving 25–67% yields of the desired adducts after purification.

Benzyne adds easily to 9-substituted anthracene derivatives[110] and the adducts from these reactions have been used in the preparation of pyrazole-containing ferrocenyl ligands for asymmetric catalysis[111] and as templates for the oligoselective polymerisation of acrylate monomers.[112] This triptycene building block has also found application in several areas of nanotechnology such as in the preparation of metallocene molecular gears,[113] a molecular barrow[114] and a molecular ratchet.[115]

Fewer examples exist of the use of 9-substituted anthracene derivatives in natural product syntheses, presumably due to the issues regarding the regioselectivity of the Diels–Alder reaction. However, 9-[(benzyloxy)methoxy]anthracene was used as a protecting group in the first stereospecific synthesis of (±)-conduritol A.[116]

Diastereomeric control has been employed with 9-anthrylcarbinol derivatives that have been used as chiral auxiliaries in asymmetric 1,3-dipolar cycloaddition reactions.[117,118] In this study, the acrylates **48** were reacted with 1-pyrrolidine-1-oxide **49** to produce a complex mixture of all possible regio- and stereoisomers for each anthracene derivative **48** used (ranging from six to eight adducts, depending on the substituent R) (Scheme 15). In all cases, the regioselectivity favoured the formation of the adducts **50** [i.e. the ratio of 50:51 was, for R=CF_3, 59:41 (56% yield), for R=*t*-Bu, 88:12 (59% yield) and for R=Me, 79:21 (66% yield)].

More recently, highly-diastereoselective additions of maleic anhydride and *N*-methyl maleimide to the chiral 9-substituted carbinol derivatives **52** and **53** have been reported (Fig. 3).[119–121] When the carbinol **53** was employed, a reversal of the sense of diastereoselectivity was noted and this was attributed to hydrogen bonding effects overriding the inherent electrostatic interactions responsible for controlling the selectivity observed with the ether **52**.

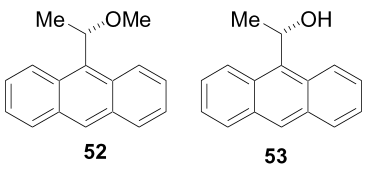
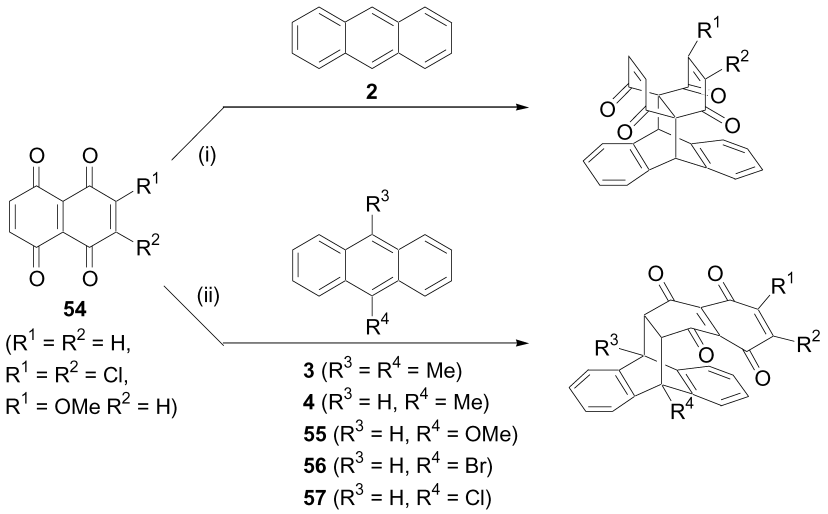


Figure 3.

3.3. Additions to 9,10-disubstituted anthracene

The first investigations into the use of 9,10-disubstituted anthracene derivatives in thermal Diels–Alder cycloaddition reactions were to compare the site selectivity of the Diels–Alder reactions of anthracene, 9-substituted and 9,10-disubstituted anthracene derivatives with naphthodiquinones.[122] It was shown that anthracene **2** reacted with derivatives of naphthodiquinone **54** at the doubly-activated internal double bond of the naphthodiquinone, giving a maximum p orbital overlap by FMO considerations. The more-sterically-hindered 9-substituted and 9,10-disubstituted anthracene derivatives **3**, **4**, **55**, **56** and **57** reacted with the unsubstituted terminal double bond of the naphthodiquinone via a less-sterically-hindered transition state (Scheme 16). Further Diels–Alder reactions were carried out on the addition products (where R^1=R^2=H), in order to investigate the use of anthracene as a protecting and/or directing group for naphthodiquinones. Lewis acid-catalysed cycloreversions were also performed.

In order to assess the effect of substituents upon the rate of the retro Diels–Alder reaction, adducts of anthracene and



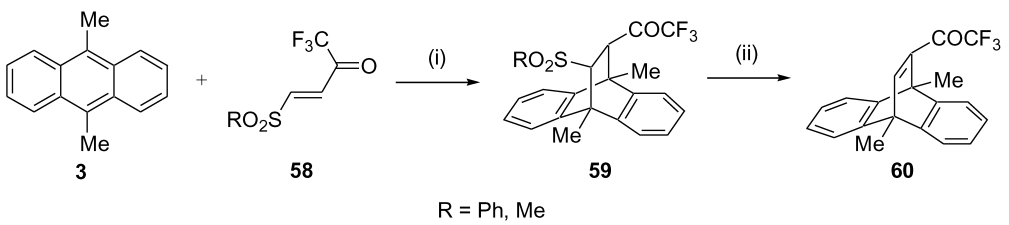
Scheme 16. *Reagents and conditions*: (i) dry C_6H_6 or $CHCl_3$, rt; (ii) dry $CHCl_3$, rt.

9,10-disubstituted anthracene derivatives were synthesised via reflux for 16 to 96 h in either the neat dienophile or a xylene solution (with small amounts of hydroquinone or BHT added), with yields ranging from 3 to 93%.[123] In another study, the thermal cycloaddition reaction of a 9,10-disubstituted anthracene derivative was used to investigate the possibility of inter-bead reactions of polystyrene resin beads.[124] The reactions of beads with bound 9,10-disubstituted anthracene and beads with bound maleimide were carried out in toluene and DMF. Aggregation of the beads was noted, showing an inter-bead cycloaddition reaction to have occurred.

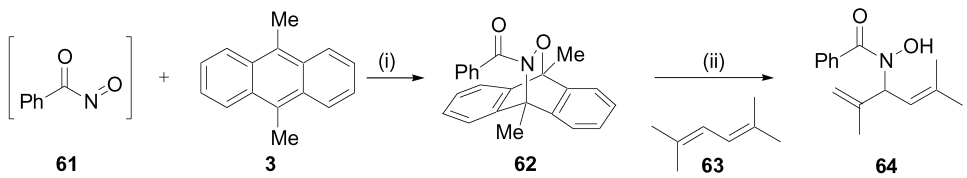
9,10-Dimethylanthracene **3** and β-trifluoroacetylvinyl-sulphone **58** have been shown to react by refluxing in CH_2Cl_2, giving 70 to 72% of the *trans*-adducts **59** (Scheme 17).[125] The relatively mild conditions used were due to the high reactivity of this type of dienophile, resulting from the CF_3 group lowering the energy of the LUMO. Subsequent elimination of the sulphonyl group by DBU yielded an α,β-unsaturated trifluoromethylketone **60** in good yield.

Reports of thermal Diels–Alder cycloadditions of alkenes and alkynes to 9,10-disubstituted anthracene derivatives are limited, although, once again, 3-phenylsulphonylprop-2-enenitrile has been used as a cyanoacetylene equivalent.[125] Addition of benzyne to 9-acetoxyanthracene and 9,10-dibromoanthracene followed by fluorination was performed to investigate the ^{19}F substituent chemical shifts.[126] 9,10-Dimethylanthracene was used to trap benzyne and thus prove the intermediacy of the latter compound in the aprotic diazotisation of an aniline.[127] The thermal addition of benzyne to 9,10-anthracenocrown ethers by refluxing for 6 h in CH_2Cl_2 produced the first triptycenocrown ethers that were used to prepare thallium complexes that provided information on the geometrical features of this type of host system.[128] The reaction of C_{60} with 9,10-dimethylanthracene was found to establish an equilibrium between the Diels–Alder adducts C_{60}(9,10-dimethylanthracene)$_n$, the stoichiometry of which was dependent on the concentration of 9,10-dimethylanthracene.[129] The anthracene derivatives could be removed from the equilibrium by reaction with oxygen (under laboratory light) or dimethyl acetylenedicarboxylate that yielded the corresponding cycloadducts of 9,10-dimethylanthracene and unmodified C_{60}.

As with anthracene, the thermal hetero Diels–Alder reactions of transient thioaldehydes with 9,10-dimethylanthracene in toluene have been carried out to produce stable cycloadducts that were later cleaved under thermal conditions to release the thioaldehydes for further reaction.[74,75] Hetero Diels–Alder reactions of transient nitrosocarbonyl compounds (e.g. **61**), produced in situ by the oxidation of hydroxamic acids, with various 9,10-disubstituted anthracene derivatives have been well documented.[130–138] The retro Diels–Alder reaction has then been used to free the nitrosocarbonyl compounds for further reaction. For example, the cycloadduct **62** obtained from 9,10-dimethylanthracene **3** was cleaved thermally to yield the nitrosocarbonyl compound **61**, which immediately underwent an intermolecular 'ene' reaction with 2,5-dimethylhexa-2,4-diene **63** to give the hydroxamic acid **64**



Scheme 17. *Reagents and conditions*: (i) CH_2Cl_2, △; (ii) DBU, CH_2Cl_2, rt.



Scheme 18. *Reagents and conditions*: (i) benzohydroxamic acid, CH_2Cl_2, Et_4NIO_4; (ii) C_6H_6, 80°C, 5 h.

in 94% yield (Scheme 18).[133] This methodology has been used successfully in the total synthesis of the marine alkaloids (±)-fasicularin and (±)-lepadiformine.[135,136] Similarly, *N*-hydroxycarbamic esters **65** and *N*-hydroxyureas **66** (Fig. 4) have been oxidised to form transient *C*-nitrosoformate esters and *C*-nitrosoformamides, which have been 'trapped' via a hetero Diels–Alder reaction with 9,10-dimethylanthracene to give stable cycloadducts.[139–141] The thermal cleavage of cycloadducts derived from various *N*-hydroxyureas at 40°C in aqueous solution was shown to produce nitrous oxide, indicating the intermediary nitroxyl (HNO), a compound of biological importance.[141]

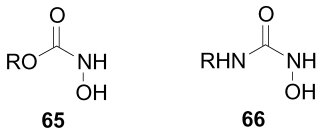


Figure 4.

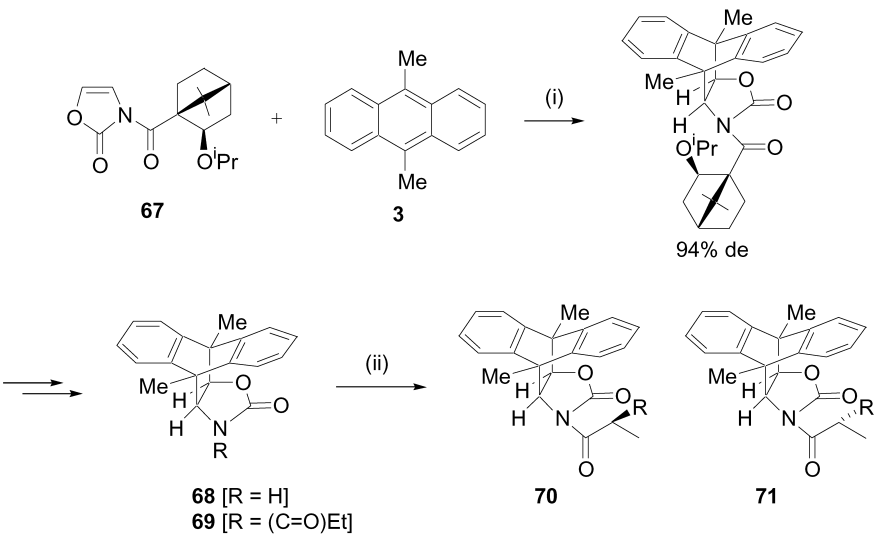
The thermal hetero Diels–Alder reaction of 9,10-dimethylanthracene has also been used in the production of pure nitrosyl cyanide (ONCN).[142] This compound is usually prepared by the reaction of nitrosyl chloride and solid silver cyanide at −25°C, but the nitrosyl cyanide contains impurities such as nitrosyl chloride and nitrosyl dioxide. Cleavage of the purified cycloadduct from the reaction of impure nitrosyl cyanide gas and a solution of 9,10-dimethylanthracene generates pure nitrosyl cyanide.

Stereoselective reactions of 9,10-disubstituted anthracene derivatives are uncommon. However, a chiral dienophile **67** has been used to control the diastereoselectivity of a [4+2] cycloaddition reaction with 9,10-dimethylanthracene **3** to give, after synthetic manipulation, the chiral auxiliary **68** in up to 94% de.[143,144] Subsequent alkylation reactions of *N*-acyl derivatives of the auxiliary **69** gave diastereoselectivities in excess of 500:1 (**70/71**) when RX was $PhCH_2Br$, $CH_2{=}CHCH_2Br$ and EtI (Scheme 19). The analogous reactions with Evans' auxiliary gave selectivities in the range 16:1 to 99:1.[145]

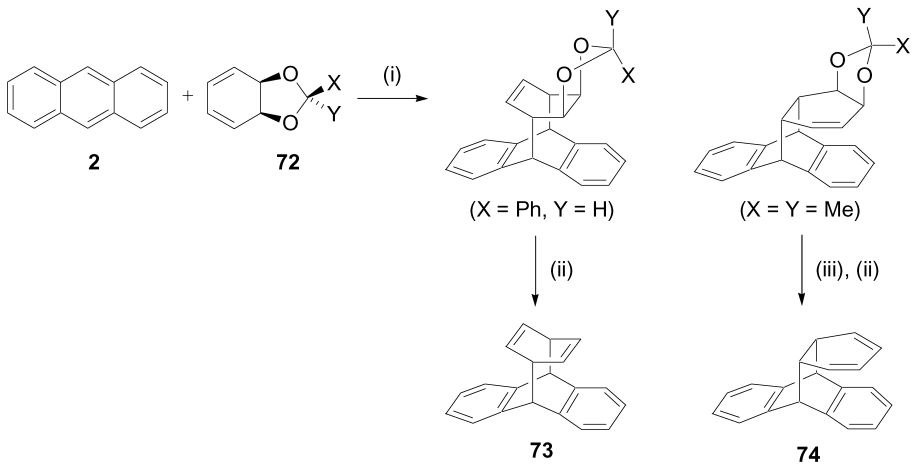
4. Photochemical Diels–Alder reactions

4.1. Additions to anthracene

Many of the photochemical studies into the cycloaddition reactions of anthracene have been concerned with the mechanism of the process and have been discussed earlier. A study of the photochemical Diels–Alder and retro Diels–Alder reactions of anthracene has been performed using anthracene **2** and substituted 2,4-cyclohexadiene derivatives **72** to give the [4+4] addition product **73** and the [4+2] addition product **74** (Scheme 20).[146] The chemoselectivity of the photocycloaddition was controlled by the choice of substrate and experimental conditions. The [4+4] addition was carried out in CH_2Cl_2, whereas the [4+2] addition was carried out in acetonitrile. The [4+2] addition was thought to occur via a stepwise mechanism, as a concerted mechanism was disfavoured by the Woodward–Hoffmann rules. The rationale behind the choice of substrate and experimental conditions to influence the outcome of the cycloaddition reactions was not discussed.



Scheme 19. *Reagents and conditions*: (i) *m*-xylene, △; (ii) LDA, RX.

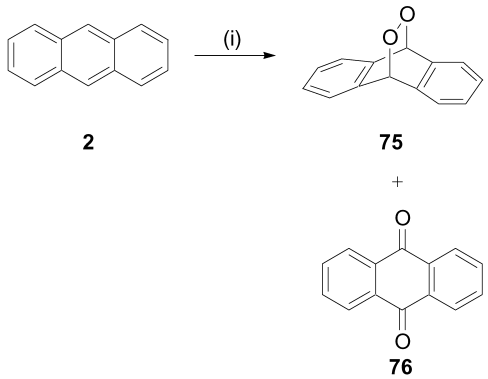


2 72 73 74

Scheme 20. *Reagents and conditions*: (i) $h\nu^{*}$; (ii) *t*-BuLi; (iii) H_3O^+, then $PhCH(OMe)_2$ (*no details given).

Investigations into the photocycloaddition reactions of anthracene and *trans*,*trans*-2,4-hexadiene isolated two adducts corresponding to [4+4] addition to the 9,10-positions of anthracene (ca. 86%) and an adduct corresponding to a [2+4] addition (14%).[147] The [4+4] products were formed via a singlet pathway by a concerted Woodward–Hoffmann allowed process. A significant portion of the [2+4] adduct was also found to be formed from the same singlet pathway. Whether this [2+4] adduct was formed through a concerted Woodward–Hoffmann forbidden pathway or a stepwise pathway was not reported.

Illumination of anthracene **2** in aerated water at 350 nm water gave the endoperoxide **75** and 9,10-anthraquinone **76** as the major products in a 3:1 ratio, respectively (Scheme 21).[148] However, when illuminated in oxygen-deficient aqueous solutions, anthracene **2** gave the three



2 75 76

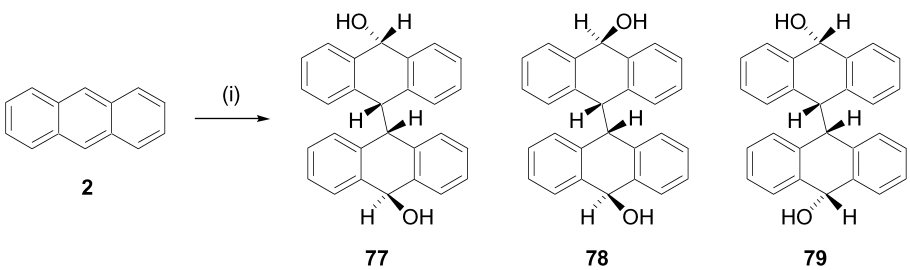
Scheme 21. *Reagents and conditions*: (i) $h\nu^{*}$, H_2O, O_2 (*350 nm).

isomers **77**–**79** as the primary products in a ratio of 3:3:1, respectively (Scheme 22). A mechanism proceeding via an anthryl cationic radical intermediate was postulated.

4.2. Additions to 9-substituted anthracene

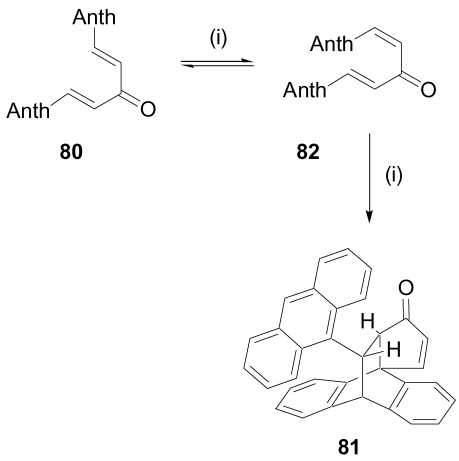
Once again, many of the photochemical studies of Diels–Alder cycloaddition reactions of 9-substituted anthracene derivatives have been concerned with the mechanism of the process. Investigations into the stereochemical outcome of the photochemical cycloaddition reactions of 9-substituted anthracene have been carried out using the intramolecular photochemical [4+2] cycloadditions of 'tethered' dienophiles. A suspension of (*E*,*E*)-1,5-bis(9-anthryl)penta-1,4-dien-3-one **80** in methylene chloride was illuminated for 1 h to yield the desired adduct **81** in 82% yield after purification (Scheme 23).[149] The reaction was found to proceed via the isomerisation of the starting material to an excited state (*E*,*Z*)-isomer **82** to give the *trans* adduct which was confirmed using X-ray diffraction studies. The use of (9-anthryl)methyl methyl fumarate in a tethered photochemical cycloaddition gave a 66% yield of the desired addition product,[150] an improvement on the untethered reaction that required a high concentration of dimethyl fumarate.[25,26] The *cis* isomer was not detected and no dimer was formed.

The solid-state photochemical [4+2] cycloaddition reaction of 9-methylanthracene with C_{60} has also been investigated.[151] A well-ground mixture of the reactants was irradiated, producing 30% of the mono-adduct **83** (Fig. 5) and 19% of a bis-adduct, the exact isomer of which was not



2 77 78 79

Scheme 22. *Reagents and conditions*: (i) $h\nu^{*}$, H_2O, Ar purged (*350 nm).



Scheme 23. *Reagents and conditions*: (i) $h\nu^{*}$, $CHCl_2$, 18°C, 1 h (*125 W high-pressure Hg lamp, pyrex immersion well apparatus, 400 nm cut-off.

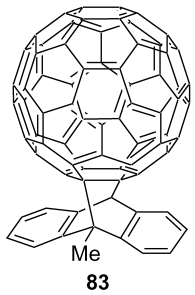
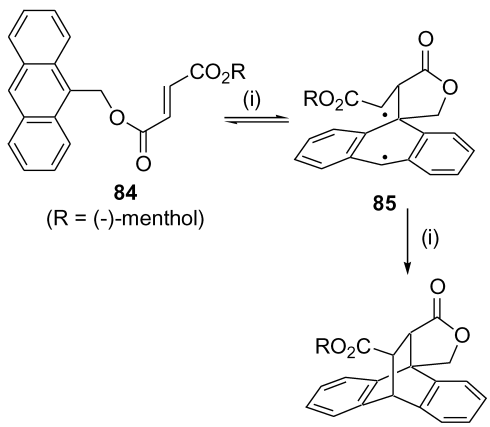


Figure 5.

identified. However, anthracene did not react under these conditions, a fact which was attributed to the lower ionisation potential of substituted anthracene derivatives. It was proposed that the reaction proceeded via photo-induced single-electron transfer from the anthracene derivatives to the triplet excited state of C_{60}.

Asymmetric induction in the [4+2] cycloaddition reaction of (9-anthryl)methyl menthyl fumarate **84** under similar conditions was also investigated by Okada's group,[150] giving a diastereomeric ratio of 76:24 after optimisation of the reaction conditions (Scheme 24). The reaction was proposed to occur via a diradical intermediate **85**, where



Scheme 24. *Reagents and conditions*: (i) $h\nu^{*}$, C_6H_5Me, −20°C (*450 W high-pressure Hg lamp, pyrex filter).

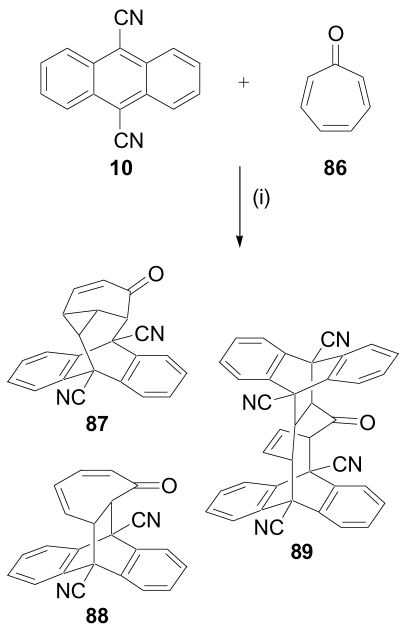
formation of the first C–C bond was fast and reversible. The stereodifferentiation was thought to mainly operate in the formation of the second bond, where the stereogenic centre was close to the reaction centre.

Illumination of a solution of anthracene and cyclohexadiene in benzene resulted in a concerted, stereospecific photochemical electrocyclic [4+4] cycloaddition reaction.[152] The same result was obtained when *trans*,*trans*-2,4-hexadiene was used instead of cyclohexadiene. No Diels–Alder adducts were noted in these reactions, but subsequent studies using 9-substituted anthracene derivatives obtained stereospecific photochemical [4+2] cycloaddition products along with small amounts, of the anthracene dimer.[153] It was postulated that the stereospecificity observed in these reactions suggested that the course of the photochemical addition reaction may be controlled by the configuration of the reacting components in an exciplex intermediate.

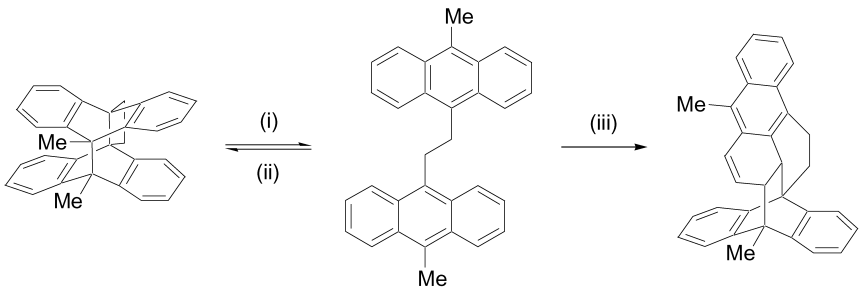
Diastereoselective photochemical cycloadditions of the carbinol derivatives **52** and **53** with maleic anhydride and *N*-methyl maleimide (Fig. 3) have also been reported.[119–121,154]

4.3. Additions to 9,10-disubstituted anthracene

Studies into the photochemical Diels–Alder reactions of 9,10-disubstituted anthracene derivatives are limited. The photochemical reaction of tropone **86** with 9,10-dicyanoanthracene **10** in benzene to give a mixture of adducts has been carried out (Scheme 25).[155] Although no ratio of adducts was given, they were characterised as the *meta*-cycloadduct **87**, the *trans* [4+2] cycloadduct **88** and the [4+4]-[4+2] cycloadduct **89**. The same reaction carried out in a mixed solution of $MeCN–CH_2Cl_2$ instead of benzene gave the above adducts in addition to a [4+4] adduct, formed via an electron-transfer mechanism.



Scheme 25. *Reagents and conditions*: (i) $h\nu^{*}$, C_6H_6 (*400 W high-pressure Hg lamp, >400 nm).



Scheme 26. *Reagents and conditions*: (i) $h\nu^{*}$; (ii) △; (iii) $h\nu^{**}$, C_6H_6, 70°C, 16 h (*no details given; ** 125 W high-pressure Hg lamp, >360 nm).

Other studies have examined the intramolecular Diels–Alder cycloaddition reactions of dianthrylethanes. It has been shown that illumination of dianthrylethanes such as **90** resulted in the formation of the [4+4] dimer **91** which was thermally unstable with a half life of 33 min at 25°C. However, illumination at >360 nm resulted in an intramolecular Diels–Alder cycloaddition reaction giving the [4+2] adduct **92** exclusively (Scheme 26).[156] A [4+2] product was also obtained when biacetyl was added as a sensitiser to the reaction mixture.[157]

The photochemical hetero Diels–Alder reaction of 9,10-diphenylanthracene with singlet oxygen gave the endoperoxide **93** (Fig. 6) using haematoporphyrin (illuminated at ≥470 nm)[158] and zinc-*seco*-porphyrazine (using ambient laboratory lighting)[159] as photosensitisers for the formation of the singlet oxygen. However, further application of this methodology was limited as only relatively poor yields (40 and 20%, respectively) of the endoperoxide were obtained.

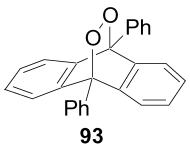


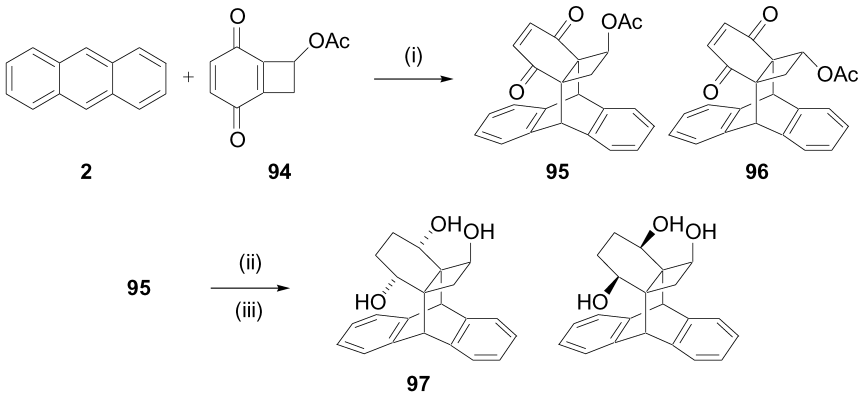
Figure 6.

5. Lewis acid-catalysed Diels–Alder reactions

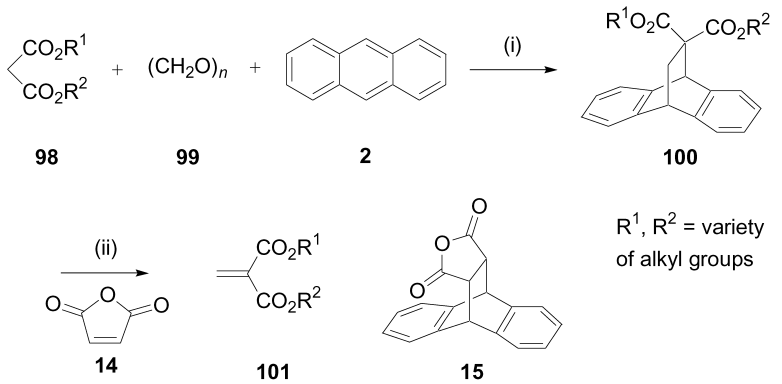
5.1. Additions to anthracene

Slow reaction times with poor dienophiles coupled with high reaction temperatures have prompted investigations into the use of Lewis acid catalysts for the Diels–Alder reactions of anthracene. One of the first investigations into the use of Lewis acids noted large increases in the rate of reaction when 1 equiv. of $AlCl_3$ was used in the reaction of anthracene and maleic anhydride in CH_2Cl_2.[160] The reaction was found to be complete in 1.5 min compared to an estimated 4800 h under the same conditions, but without $AlCl_3$. Similar rate increases were noted for the reactions of anthracene and *p*-benzoquinone, diethyl maleate, diethyl fumarate, citraconic anhydride and dichloromaleic anhydride. $AlCl_3$ has also been used to catalyse the Diels–Alder additions of isothiazoles to anthracene at 130–140°C, although the products were obtained in low yields.[161] The addition of a chiral sulphinyl acrylate to anthracene was carried out in CH_2Cl_2 using $ZnCl_2$ as a catalyst, producing the desired adduct in 81% yield and in excellent diastereoselectivity.[162] Other chiral dienophiles used in Lewis acid-catalysed cycloaddition reactions include 4-hydroxycyclopentenones ($AlCl_3$ catalyst, 83% yield, 94% ee)[163] and both enantiomers of 3-hydroxypyrrolidinones ($TiCl_4$ catalyst, 87% yield, >99% ee).[164] $Sc(OTf)_3$ has enjoyed considerable success as a catalyst when using benzoquinone as the substrate,[165] as have aluminosilicates.[166]

The cycloadditions of alkenes and alkynes have also been carried out using Lewis acid catalysis including the addition of a physically-constrained cycloheptatetraene to anthracene employing a catalytic amount of SeO_2.[167] The addition of the acetoxyquinone **94** to anthracene **2** was achieved in the presence of $BF_3{\cdot}OEt_2$ to produce the stereoisomers **95** and **96** in 83% yield (no ratio given, Scheme 27).[168] The anthracene ring system was then used to control the selectivity of the reduction of the major isomer **95** using $LiAlH_4$, to give the triol **97** in 91% yield and a dr of 3.6:1.



Scheme 27. *Reagents and conditions*: (i) $BF_3{\cdot}OEt_2$, C_6H_6, rt, 5 h; (ii) Zn, AcOH, 60°C; (iii) $LiAlH_4$, THF, 0°C.



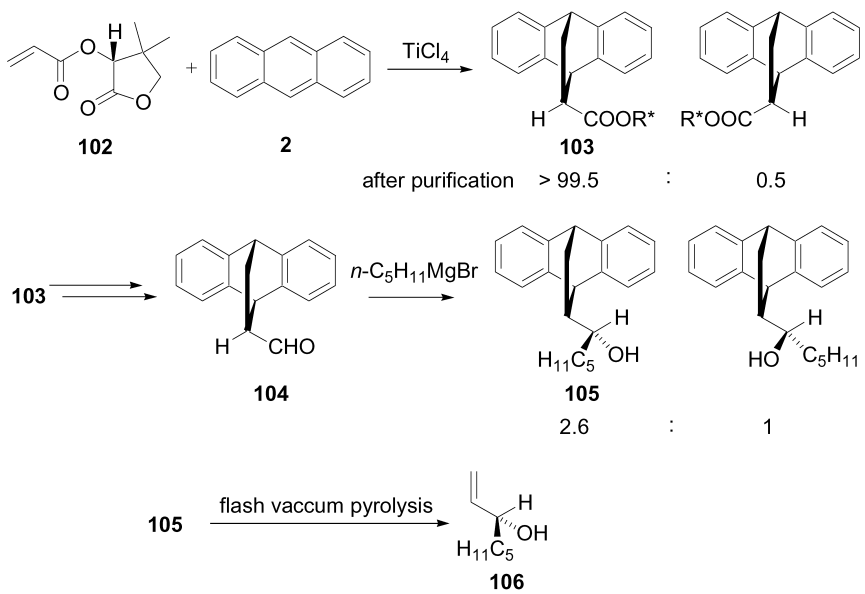
Scheme 28. *Reagents and conditions*: (i) $Cu(OAc)_2$, AcOH, xylene, 100°C, 2 h; (ii) △, 45 min.

The applicability of the Lewis acid-catalysed cycloaddition reaction of anthracene has been demonstrated in the synthesis of methylidenemalonic acid diesters.[169] A mixture of the dialkyl malonate **98**, paraformaldehyde **99** and anthracene **2** was heated in xylene and acetic acid in the presence of $Cu(OAc)_2$, affording the desired addition products **100** in 41–84% yield. Thermolysis of the addition adducts in the presence of maleic anhydride **14** gave the methylidenemalonic acid diesters **101** in good yields (Scheme 28). Maleic anhydride was used to trap the anthracene produced as the anthracene–maleic anhydride adduct **15**. Similarly, $AlCl_3$ has been used as a catalyst for the cycloaddition reactions of anthracene in the preparation of iptycenes[170] and triptycenes.[171]

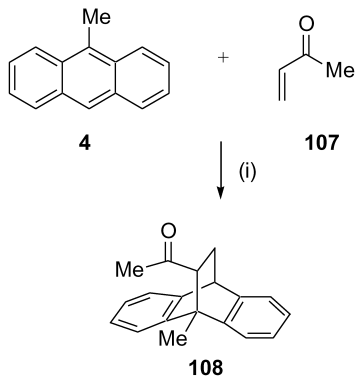
A chiral auxiliary approach has been used to prepare a sterically-constrained β-amino acid by a Lewis acid-catalysed reaction of anthracene with dimenthyl fumarate.[172] The addition product was obtained in 88% yield and 99% ee. Asymmetric synthesis has also been carried out using anthracene as a stereodirecting group. Helmchen et al. were one of the first groups to carry out a highly-diastereoselective $TiCl_4$-promoted addition reaction of a chiral acrylate **102** to anthracene **2**.[173] The isolated addition product **103** was converted in a series of transformations to an aldehyde **104** that was used as a substrate for Grignard additions that proceeded with reasonable levels of selectivity (Scheme 29). After separation of the major isomer **105**, flash vacuum pyrolysis was used to initiate a retro Diels–Alder reaction, giving the desired product **106** without any detectable racemisation. The main drawback of this methodology was that a stereodirecting group on the alkene was used to control the diastereoselectivity of the addition step. Although excellent selectivity was achieved, the initial addition adduct required several steps to transform it into the desired substrate for the Grignard addition.

5.2. Additions to 9-substituted anthracene

The attempted cycloaddition of 9-substituted anthracene derivatives with methyl vinyl ketone **107** returned the starting materials in the absence of a catalyst. However, a single regioisomer **108** was formed with 9-methylanthracene



Scheme 29.



Scheme 30. *Reagents and conditions*: (i) MeCN, $Sc(OTf)_3$, rt.

4 in the presence of $Sc(OTf)_3$ at room temperature (Scheme 30).[174] This catalyst has also been successfully employed in Diels–Alder reactions with benzoquinone.[165]

A number of chiral carbinol-derived 9-substituted anthracene derivatives have been used in the $Cu(OTf)_2$-catalysed Diels–Alder cycloadditions with a variety of symmetrical and non-symmetrical dienophiles with good diastereoselectivity and regioselectivity.[175] The origins of the selectivity were shown to be electrostatic repulsions between the dienophile carbonyl oxygen atom and the alkoxy oxygen atom on the C-9 substituent. Subsequent studies into the facial selectivity of the Diels–Alder cycloaddition reaction and the acceleration of this reaction by additional substitution in the C-10 position of anthracene were also carried out.[176]

5.3. Additions to 9,10-disubstituted anthracene

Examples of Lewis acid-catalysed Diels–Alder cycloaddition reactions with 9,10-disubstituted anthracene derivatives are limited. The addition of $Mg(ClO_4)_2$ to a solution of *p*-benzoquinone and 9,10-dimethylanthracene in acetonitrile at room temperature has been found to vastly increase the rate of the cycloaddition reaction which, without catalysis, was very sluggish.[177] Similar results were obtained with $Sc(OTf)_3$.[165]

References

1. See Lotfi, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2131–2136, and references therein.
2. Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183–3207.
3. Lotfi, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2137–2141.
4. Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036–4039.
5. Hayakawa, K.; Mibu, N.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1982**, *104*, 7136–7142.
6. Sauer, J.; Sustmann, R. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779–807.
7. Desimoni, G.; Faita, G.; Righetti, P. P.; Toma, L. *Tetrahedron* **1990**, *46*, 7951–7970.
8. Cativiela, C.; Garcia, J. I.; Mayoral, J. A.; Salvatella, L. *Chem. Soc. Rev.* **1996**, 209–218.
9. Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325–1334.
10. Kumar, A.; Pawar, S. S. *J. Org. Chem.* **2001**, *66*, 7646–7652.
11. Kumar, A.; Pawar, S. S. *Tetrahedron* **2002**, *58*, 1745–1749.
12. Myers, K. E.; Kumar, K. *J. Am. Chem. Soc.* **2000**, *122*, 12025–12026.
13. Vaughan, W. R.; Andersen, K. S. *J. Org. Chem.* **1956**, *21*, 673–683.
14. Dudkowski, J. J.; Becker, E. I. *J. Org. Chem.* **1952**, *17*, 201–206.
15. Vaughan, W. R.; Milton, K. M. *J. Org. Chem.* **1951**, *16*, 1748–1752.
16. Bachmann, W. E.; Kloetzel, M. C. *J. Am. Chem. Soc.* **1938**, *60*, 481–485.
17. Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 6284–6289.
18. Andrews, L. J. *Chem. Rev.* **1954**, *54*, 713–776.
19. Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43–55.
20. Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145–172.
21. Roth, H. D. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1193–1207.
22. Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P. *Pure Appl. Chem.* **1980**, *52*, 2633–2633.
23. Epiotis, N. D.; Yates, R. L. *J. Org. Chem.* **1974**, *39*, 3150–3153.
24. Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781–853.
25. Kaupp, G. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 313–314.
26. Kaupp, G. *Liebigs Ann. Chem.* **1977**, 254–275.
27. Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162–4172.
28. Yang, N.-C. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* **1979**, *51*, 173–180.
29. Diels, O.; Alder, K. *Ann.* **1931**, *486*, 191–202.
30. Clar, E. *Ber.* **1931**, *64*, 2194–2200.
31. Bachmann, W. E.; Scott, L. B. *J. Am. Chem. Soc.* **1948**, *70*, 1458–1461.
32. Hall, H. K.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* **1982**, *47*, 1451–1455.
33. Anderson, W. K.; Milowsky, A. S. *J. Org. Chem.* **1985**, *50*, 5423–5424.
34. Giguere, R. J.; Bray, T. L.; Duncan, S. M. *Tetrahedron Lett.* **1986**, *27*, 4945–4948.
35. Bose, A. K.; Manhas, M. S.; Ghosh, M.; Shah, M.; Raju, V. S.; Bari, S. S.; Newaz, S. N.; Banik, B. K.; Chaudhary, A. G.; Barakat, K. J. *J. Org. Chem.* **1991**, *56*, 6968–6970.
36. Rongshun, Z.; Pinjie, H.; Shushan, D. *Synth. Commun.* **1994**, *24*, 2417–2421.
37. Garrigues, B.; Laporte, C.; Laurent, R.; Laporterie, A.; Dubac, J. *Liebigs Ann.* **1996**, 739–741.
38. Mataka, S.; Ma, J.; Thiemann, T.; Rudzinski, J. M.; Tsuzuki, H.; Sawada, T.; Tashiro, M. *Tetrahedron* **1997**, *53*, 885–902.
39. Garrigues, P.; Garrigues, B. *Org. Organomet. Synth.* **1998**, 545–550.
40. Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.
41. Szmant, H. H.; Nanjundiah, R. *J. Org. Chem.* **1978**, *43*, 1835–1837.
42. Hosokawa, T.; Aoki, S.; Murahashi, S.-I. *Synthesis* **1992**, 558–561.
43. Allenmark, S.; Skogsberg, U.; Thunberg, L. *Tetrahedron: Asymmetry* **2000**, *11*, 3527–3534.

44. Hurd, C. D.; Tockman, A. *J. Am. Chem. Soc.* **1959**, *81*, 116–119.
45. Diels, O.; Friedrichsen, W. *Liebigs Ann. Chem.* **1934**, *513*, 145–155.
46. Weber, E.; Csoregh, I.; Ahrendt, J.; Finge, S.; Czugler, M. *J. Org. Chem.* **1988**, *53*, 5831–5839.
47. Mowry, D. T. *J. Am. Chem. Soc.* **1947**, *69*, 573–575.
48. Barnett, E. B.; Goodway, N. F.; Weekes, E. V. *J. Chem. Soc.* **1935**, 1102–1104.
49. Bartlett, P. D.; Tate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91–95.
50. Jackson, Y. A.; Hepburn, S. A.; Reynolds, W. F. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2237–2239.
51. Hoz, A.; Díaz-Ortis, A.; Moreno, A.; Langa, F. *Eur. J. Org. Chem.* **2000**, 3659–3673.
52. Noland, W. E. *Chem. Rev.* **1955**, *55*, 137–155.
53. Klager, K. *J. Org. Chem.* **1955**, *20*, 650–656.
54. Hurd, C. D.; Juel, L. H. *J. Am. Chem. Soc.* **1955**, *77*, 601–606.
55. Noland, W. E.; Freeman, H. I.; Baker, M. S. *J. Am. Chem. Soc.* **1956**, *78*, 188–192.
56. Ono, N.; Kamimura, A.; Kaji, A. *Tetrahedron Lett.* **1986**, *27*, 1595–1598.
57. Ono, N.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1988**, *53*, 251–258.
58. Ito, S.; Murashima, T.; Ono, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3161–3165.
59. Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597–1599.
60. Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976–4986.
61. Bradley, P. J.; Grayson, D. H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1794–1799.
62. Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643–4646.
63. Picker, K.; Proust, S. M.; Ridley, D. D. *Aust. J. Chem.* **1986**, *39*, 575–589.
64. Jarvis, B. B.; Yount, J. B. *J. Org. Chem.* **1970**, *35*, 2088–2090.
65. Whitney, R. A. *Tetrahedron Lett.* **1981**, *22*, 2063–2066.
66. Jung, M. E.; Buszek, K. R. *Tetrahedron Lett.* **1986**, *27*, 6165–6168.
67. Lasne, M.-C.; Ripoll, J.-L.; Thuillier, A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 99–104.
68. Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473–8476.
69. Kräutler, B.; Müller, T.; Maynollo, J.; Gruber, K.; Kratky, C.; Ochsenbein, P.; Schwarzenbach, D.; Bürgi, H.-B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1204–1206.
70. Sandall, J. P. B.; Fowler, P. W.; Taylor, R. J. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1718–1721.
71. Raymo, F. M.; Parisi, M. F.; Kohnke, F. H. *Tetrahedron Lett.* **1993**, *34*, 5331–5332.
72. Battiste, M. A.; Duan, J.-X.; Zhai, Y.-A.; Ghivirga, I.; Abboud, K. A.; Roitberg, A.; Shelton, G. R.; Dolbier, W. R., Jr. *Tetrahedron Lett.* **2002**, *43*, 7047–7049.
73. Battiste, M. A.; Duan, J.-X.; Zhai, Y.-A.; Ghivirga, I.; Abboud, K. A.; Dolbier, W. R., Jr. *J. Org. Chem.* **2003**, *68*, 3078–3083.
74. Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487–1498.
75. Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1541–1545.
76. Freer, A. A.; Kirby, G. W.; Lewis, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 718–719.
77. Capozzi, G.; Menichetti, S.; Nativi, C.; Vergamini, C. *Synthesis* **1998**, 915–918.
78. Bertilsson, S. K.; Ekegren, J. K.; Modin, S. A.; Andersson, P. G. *Tetrahedron* **2001**, *57*, 6399–6406.
79. Breton, G. W.; Shugart, J. H.; Hughey, C. A.; Perala, S. M.; Hicks, A. D. *Org. Lett.* **2001**, *3*, 3185–3187.
80. Kitamura, T.; Kawakami, Y.; Imagawa, T.; Kawanisi, M. *Tetrahedron Lett.* **1978**, *44*, 4297–4300.
81. Cambie, R. C.; Renner, N. D.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1991**, *44*, 61–75.
82. Pirkle, W. H.; Gruber, J. V. *J. Org. Chem.* **1989**, *54*, 3422–3428.
83. Tarnchompoo, B.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1987**, *28*, 6671–6674.
84. Nozaki, H.; Kato, H.; Noyori, R. *Tetrahedron* **1969**, *25*, 1661–1665.
85. Siwapinyoyos, T.; Thebtaranonth, Y. *J. Org. Chem.* **1982**, *47*, 598–599.
86. Kodpinid, M.; Siwapinyoyos, T.; Thebtaranonth, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4862–4865.
87. Hakiki, A.; Jabry, Z.; Ripoll, J.-L.; Thuillier, A. *Tetrahedron Lett.* **1984**, *25*, 3461–3462.
88. Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121–143.
89. Karpf, M. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 414–430.
90. Kongsaeree, P.; Meepowpan, P.; Thebtaranonth, Y. *Tetrahedron: Asymmetry* **2001**, *12*, 1913–1922.
91. Trost, B. M.; Pulley, S. R. *Tetrahedron Lett.* **1995**, *36*, 8737–8740.
92. Lertvorachon, J.; Thebtaranonth, Y.; Thongpanchang, T.; Thongyoo, P. *J. Org. Chem.* **2001**, *66*, 4692–4694.
93. Meek, J. S.; Toon, B. T.; Cristol, S. J. *J. Am. Chem. Soc.* **1952**, 761–763.
94. Alston, P. V.; Ottenbrite, R. M.; Newby, J. *J. Org. Chem.* **1979**, *44*, 4939–4943.
95. Herndon, W. C. *Chem. Rev.* **1972**, *72*, 157–179.
96. Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 5624–5632.
97. Hudson, R. F. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 36–56.
98. Eisenstein, O.; Lefour, J. M.; Anh, N. T.; Hudson, R. F. *Tetrahedron* **1977**, *33*, 523–531.
99. Czarnik, A. W. *Tetrahedron Lett.* **1984**, *25*, 4875–4878.
100. Nanjappan, P.; Czarnik, A. W. *J. Am. Chem. Soc.* **1987**, *109*, 1826–1833.
101. Koerner, M.; Rickborn, B. *J. Org. Chem.* **1989**, *54*, 6–9.
102. Koerner, M.; Rickborn, B. *J. Org. Chem.* **1990**, *55*, 2662–2672.
103. Harrison, R.; Rickborn, B. *Org. Lett.* **2002**, *4*, 1711–1713.
104. Fache, F.; Piva, O. *Tetrahedron Lett.* **2001**, *42*, 5655–5657.
105. Seelig, B.; Keiper, S.; Stuhlmann, F.; Jaschke, A. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 4576–4579.
106. Stuhlmann, F.; Jaeschke, A. *J. Am. Chem. Soc.* **2002**, *124*, 3238–3244.
107. Ciganek, E. *J. Org. Chem.* **1980**, *45*, 1497–1505.
108. Elnagar, H. Y.; Chow, K. H.; Johnson, A. T.; Somanathan, R.; Nunez, P.; Watson, M. J.; Parsons, C. S.; Grubbs, E. J. *Tetrahedron* **1986**, *42*, 5841–5848.
109. Schuck, D. F.; Bach, D. T.; Chow, K. H.; Sullivan, R. W.; Linhares, M.; Grubbs, E. J. *J. Org. Chem.* **1991**, *56*, 1360–1364.

110. Bartlett, P. D.; Greene, P. D. *J. Am. Chem. Soc.* **1954**, *76*, 1088–1096.
111. Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A. *Organometallics* **1995**, *14*, 5415–5425.
112. Feldman, K. S.; Bobo, J. S.; Ensel, S. M.; Lee, Y. B.; Weinreb, P. H. *J. Org. Chem.* **1990**, *55*, 474–481.
113. Stevens, A. M.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 7805–7808.
114. Joachim, C.; Tang, H.; Mersco, F.; Rapenne, G.; Meyer, G. *Nanotechnology* **2002**, *13*, 330–335.
115. Kelly, T. R.; Sestelo, J. P.; Tellitu, I. *J. Org. Chem.* **1998**, *63*, 3655–3665.
116. Knapp, S.; Ornaf, R. M.; Rohriques, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 5494–5495.
117. Carriere, A.; Virgili, A. *Tetrahedron: Asymmetry* **1996**, *7*, 227–230.
118. Carriere, A.; Virgili, A.; Figueredo, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2793–2796.
119. Jones, S.; Atherton, J. C. C. A. *Tetrahedron: Asymmetry* **2000**, *12*, 1117–1119.
120. Atherton, J. C. C. A.; Jones, S. *Tetrahedron Lett.* **2001**, *42*, 8239–8241.
121. Atherton, J. C. C. A.; Jones, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2166–2173.
122. Hayakawa, K.; Aso, M.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 2036–2040.
123. Chung, Y.; Duerr, B. F.; McKelvey, T. A.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1989**, *54*, 1018–1032.
124. Thomas, I. P.; Ramsden, J. A.; Kovacs, T. Z.; Brown, J. M. *Chem. Commun.* **1999**, 1507–1508.
125. Krasovsky, A. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2001**, *57*, 201–209.
126. Adcock, W.; Iyer, V. S. *J. Org. Chem.* **1988**, *53*, 5259–5266.
127. Naghipur, A.; Reszka, K.; Sapse, A.-M.; Lown, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 258–268.
128. Gakh, A. A.; Sachleben, R. A.; Bryan, J. C.; Moyer, B. A. *Tetrahedron Lett.* **1995**, *36*, 8163–8166.
129. Lamparth, I.; Maichle-Mossmer, C.; Hirsch, A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1607–1609.
130. Kirby, G. W.; Sweeny, J. G. *J. Chem. Soc., Chem. Commun.* **1973**, 704–705.
131. Corrie, J. E. T.; Kirby, G. W.; Sharma, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 915–916.
132. Kirby, G. W. *Chem. Soc. Rev.* **1977**, *6*, 1–24.
133. Corrie, J. E. T.; Kirby, G. W.; Mackinnon, W. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 883–886.
134. Kirby, G. W.; Sweeny, J. G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3250–3254.
135. Abe, H.; Aoyagi, S.; Kibayashi, C. *J. Am. Chem. Soc.* **2000**, *122*, 4583–4592.
136. Abe, H.; Aoyagi, S.; Kibayashi, C. *Tetrahedron Lett.* **2000**, *41*, 1205–1208.
137. Flower, K. R.; Lightfoot, A. P.; Wan, H.; Whiting, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2058–2064.
138. Ware, R. W., Jr.; King, S. B. *J. Org. Chem.* **2000**, *65*, 8725–8729.
139. Kirby, G. W.; McGuigan, H.; Mackinnin, J. W. M.; McLean, D.; Sharma, R. P. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1437–1442.
140. Christie, C. C.; Kirby, G. W.; McGuigan, H.; Mackinnon, J. W. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2469–2473.
141. Xu, Y.; Alavanja, M.-M.; Johnson, V. L.; Yasaki, G.; King, S. B. *Tetrahedron Lett.* **2000**, *41*, 4265–4269.
142. Horsewood, P.; Kirby, G. W.; Sharma, R. P.; Sweeny, J. G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1802–1806.
143. Matsunaga, H.; Kimura, K.; Ishizuka, T.; Haratake, M.; Kunieda, T. *Tetrahedron Lett.* **1991**, *32*, 7715–7718.
144. Kimura, K.; Murata, K.; Otsuka, K.; Ishizuka, T.; Haratake, M.; Kunieda, T. *Tetrahedron Lett.* **1992**, *33*, 4461–4464.
145. Evans, D. A.; Chapman, K. T.; Hung, D. T.; Kawaguchi, A. T. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1184–1186.
146. Yang, N.-C. C.; Chen, M.-J.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 853–855.
147. Saltiel, J.; Dabestani, R.; Schanze, K. S.; Trojan, D.; Townsend, D. E.; Goedken, V. L. *J. Am. Chem. Soc.* **1986**, *108*, 2674–2687.
148. Sigman, M. E.; Zingg, S. P.; Pagni, R. M.; Burns, J. H. *Tetrahedron Lett.* **1991**, *32*, 5737–5740.
149. Becker, H.-D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1471–1480.
150. Okada, K.; Samizo, F.; Oda, M. *Tetrahedron Lett.* **1987**, *28*, 3819–3822.
151. Mikami, K.; Matsumoto, S.; Tonoi, T.; Okubo, Y. *Tetrahedron Lett.* **1998**, *39*, 3733–3736.
152. Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 1405–1406.
153. Yang, N. C.; Libman, J.; Barrett, L.; Hui, H. H.; Loeschen, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 1406–1408.
154. Atherton, J. C. C. A.; Jones, S. *Tetrahedron Lett.* **2002**, *43*, 9097–9100.
155. Wu, S.; Mori, A.; Takeshita, H. *J. Chem. Soc., Chem. Commun.* **1994**, 919–920.
156. Becker, H.-D.; Andersson, K. *Tetrahedron Lett.* **1983**, *24*, 3273–3276.
157. Becker, H.-D.; Andersson, K. *Tetrahedron Lett.* **1985**, *26*, 6129–6132.
158. Rigaudy, J.; Scribe, P.; Brelière, C. *Tetrahedron* **1981**, *37*, 2585–2593.
159. Trabanco, A. A.; Montalban, A. G.; Rumbles, G.; Barrett, A. G. M.; Hoffman, B. M. *Synlett* **2000**, 1010–1012.
160. Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436–4437.
161. Weiler, E. D.; Brennan, J. J. *J. Heterocycl. Chem.* **1978**, *15*, 1299–1302.
162. Arai, Y.; Kuwayama, S.-I.; Takeuchi, Y.; Koizumi, T. *Tetrahedron Lett.* **1985**, *26*, 6205–6208.
163. Dols, P. P. M. A.; Kluder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1994**, *50*, 8515–8538.
164. Camps, P.; Font-Bardia, M.; Giménez, S.; Pérez, F.; Solans, X.; Soldevilla, N. *Tetrahedron: Asymmetry* **1999**, *10*, 3123–3138.
165. Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147–14155.
166. Kugita, T.; Ezawa, M.; Owada, T.; Tomita, Y.; Namba, S.; Hashimoto, N.; Onaka, M. *Microporus Mesoporus Mater.* **2001**, *44-45*, 531–536.
167. Tivakornpannarai, S.; Waali, E. E. *J. Am. Chem. Soc.* **1986**, *108*, 6058–6059.
168. Okada, K.; Kawai, H.; Oda, M. *Tetrahedron Lett.* **1992**, *33*, 257–260.
169. Keyser, J.-L. D.; Cock, J. C. D.; Poupaert, J. H.; Dumont, P. *J. Org. Chem.* **1988**, *53*, 4859–4862.
170. Chen, Y.-S.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2612–2615.
171. Patney, H. K. *Synthesis* **1991**, 694–696.
172. Winkler, J. D.; Piatnitski, E. L.; Mehlmann, J.; Kasparec, J.; Axelsen, P. H. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 743–745.

173. Helmchen, G.; Ihrig, K.; Schindler, H. *Tetrahedron Lett.* **1987**, *28*, 183–186.
174. Miyagawa, T.; Suenobu, T.; Itoh, S.; Fukuzumi, S. *Kidorui* **1997**, *30*, 298–299.
175. Sanyal, A.; Snyder, J. K. *Org. Lett.* **2000**, *2*, 2527–2539.
176. Corbett, M. S.; Liu, X.; Sanyal, A.; Snyder, J. K. *Tetrahedron Lett.* **2003**, *44*, 931–935.
177. Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1993**, *115*, 11600–11601.

Biographical sketch

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Simon Jones received his first degree from the University of Southampton in 1991 developing an interest in synthetic organic chemistry which stemmed from a final year project on the total synthesis of Hernaldulcin, a sweet component of an Aztec herb. He then moved to the University of Wales, Cardiff, where he carried out his PhD under the supervision of Dr D. R. Kelly on the synthesis of nitroxide spin labelled disaccharides as novel probes to investigate the biochemical mechanism of septic shock. After this he spent a short period working at the Cancer Research Institute, Arizona State University under the supervision of Professor G. R. Pettit, investigating the synthesis of novel pro-drugs for cancer chemotherapy. He returned to the UK in 1996 to take up a postdoctoral position with Professor Steve Davies at the Dyson Perrins Laboratory, Oxford, working on several projects including photochemical transition metal chemistry, asymmetric transformations and novel rearrangements. In January 1999 he was appointed as a Lecturer in Organic Chemistry at the University of Newcastle upon Tyne to work mainly on developing new synthetic methodology, with particular emphasis in asymmetric synthesis. As of 1st June 2003, he moved to University of Sheffield to take up his current post. His research interests include Diels–Alder reactions of anthracene, developing methods for selective phosphorylation and asymmetric reduction using oxazaborolidines.