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Mechanistic investigations in diastereoselective Diels–Alder additions of chiral 9-anthrylethanol derivatives

J. C. Christian Atherton and Simon Jones *

Department of Chemistry, University of Newcastle upon Tyne, Bedson Building, Newcastle upon Tyne, UK NE1 7RU. E-mail: s.jones@ncl.ac.uk; Fax: 0191 222 6929; Tel: 0191 222 7128

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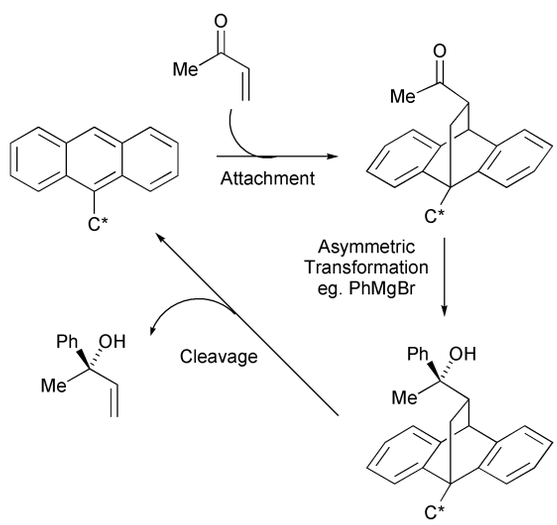
The preparation and subsequent Diels–Alder addition reactions of chiral 9-functionalised anthracene derivatives have been investigated. 9-(1-Methoxyethyl)anthracene undergoes highly diastereoselective (>95 : 5) thermal and photoinduced Diels–Alder additions with maleic anhydride and *N*-methylmaleimide. The corresponding reactions of 1-anthracen-9-ylethanol occur with the reverse sense of selectivity for additions with maleic anhydride with a corresponding increase in the reaction rate. The origins of this selectivity have been proposed to lie in hydrogen-bonding effects. The stereochemical outcome of the Diels–Alder additions has been determined from single X-ray crystallography of adducts **5** and **7**. Solvent effects on the diastereoselectivity of these reactions have also been observed.

Introduction

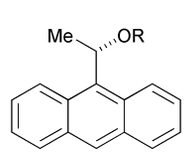
Chiral auxiliaries, such as those developed by Evans and Oppolzer, are highly versatile and undergo many asymmetric transformations.[1] However the type of asymmetric transformation that can occur with these compounds is dominated by carbonyl chemistry (*e.g.* aldol reactions, Michael additions) and may be considered to be a direct consequence of the nature of the attachment–cleavage step through formation of a carbon–nitrogen acyl bond. The use of an attachment–cleavage strategy that does not employ acyl bond formation would allow the use of a number of asymmetric transformations which are not possible with most other commonly used chiral auxiliaries.

It is well known that anthracene undergoes a thermal and photochemical Diels–Alder addition reaction with a variety of alkenes to give stable adducts that can easily be cleaved to the original starting materials by flash-vapour pyrolysis (FVP).[2] The latter reaction has been used extensively to prepare unusually substituted alkenes that are normally difficult to isolate.[3] In addition, the anthracene ring system has also been shown to act as an extremely powerful stereodirecting group in asymmetric enolate alkylations.[4] Helmchen *et al.* were one of the first groups to report a highly diastereoselective Diels–Alder addition of a chiral acrylate to anthracene, the addition product of which was converted in a series of transformations to an aldehyde that was used as a substrate for subsequent Grignard additions with good levels of diastereoselectivity.[5] Cleavage using FVP gave allylic alcohols with no loss of stereochemical integrity. The main drawback of this approach is that the stereodirecting group on the acrylate must be removed before transformation into a substrate for subsequent synthetic manipulation. A better approach would be to install the stereodirecting group into the anthracene moiety. This group would control the diastereoselectivity of the addition step, whilst the anthracene ring system would then govern the stereochemistry of any subsequent asymmetric manipulations.

Based upon these criteria, we have been developing a novel chiral auxiliary based upon functionalised 9-anthryl derivatives. These auxiliaries would make use of a diastereoselective Diels–Alder reaction of an alkene with a chiral anthracene derivative to achieve the attachment process. Subsequent asymmetric transformations of these compounds can then be carried out, followed by cleavage photochemically or by use of FVP (Scheme 1). Studies of the diastereomeric control in the addition step of this process with the carbinol derivatives **1a** and **1b** (Fig. 1) have already been disclosed by us in preliminary form,[6] and in part by another group.[7] Herein we wish to report in full our studies into the thermal and photochemical Diels–Alder addition reactions of the chiral anthryl derivative **1a** and further studies into the role of hydrogen bonding in the analogous reactions of the carbinol **1b**.



Scheme 1



1a R=Me
1b R=H

Fig. 1

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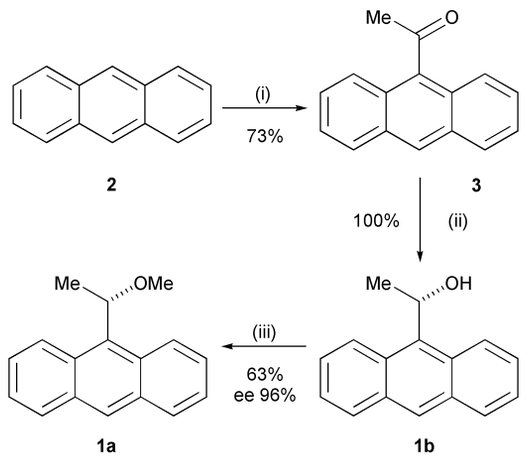
Results and discussion

Preparation of compounds

9-(1-Methoxyethyl)anthracene **1a**, our initial target auxiliary, was easily accessed in racemic and enatiomerically pure form from anthracene **2** (Scheme 2). Friedel–Crafts acetylation of



Scheme 2

anthracene **2** *via* modification of the procedure of Merritt and Braun[8] was followed by reduction of the ketone **3** with sodium borohydride to give the carbinol **1b** that could be converted to the racemic auxiliary **1a** by *O*-methylation. This route was also amenable for the preparation of the enantiomerically enriched version of this auxiliary. In the first instance, asymmetric transfer hydrogenation using the method of Wills *et al.*,[9] was unsuccessful returning only starting material, although reaction with acetophenone produced (*S*)-1-phenylethanol in excellent yield and 92% ee as reported. The use of the versatile (*S*)-2-methyl-CBS-oxazaborolidine catalyst in the asymmetric reduction of ketone **3** produced the desired alcohol **1b** in good yield but with a disappointing ee of 60% in favour of the (*R*)-enantiomer. However, previous studies with an alternative oxazaborolidine based upon (1*R*,2*S*)-1-aminoindan-2-ol led us to use this as a catalyst for the asymmetric reduction.[10] The desired alcohol **1b** was obtained as the (*S*) enantiomer in 63% ee when the ketone **3** was added dropwise *via* a dropping funnel to a solution of the pre-formed catalyst. This was increased to 68% ee when the reaction was carried out over 4 Å molecular sieves and further to 87% ee when the ketone was added *via* a syringe pump (at 0.0132 cm^3 min^{-1}). All the yields in these reductions were quantitative and the absolute configuration was determined to be (*S*) by comparison of the specific rotation of the alcohol with the literature value. The ee could be further improved by recrystallisation from petroleum ether (60–80) giving an enhanced ee (96%) with reasonable recovery of material (65%). This method appears to be one of the best of those reported in the literature to date, a close rival being through asymmetric hydrogenation giving the alcohol **1b** in 80% ee and 99% yield.[11] *O*-Methylation of the alcohol **1b** proceeded well giving the enantiomerically enriched auxiliary in excellent overall yield.

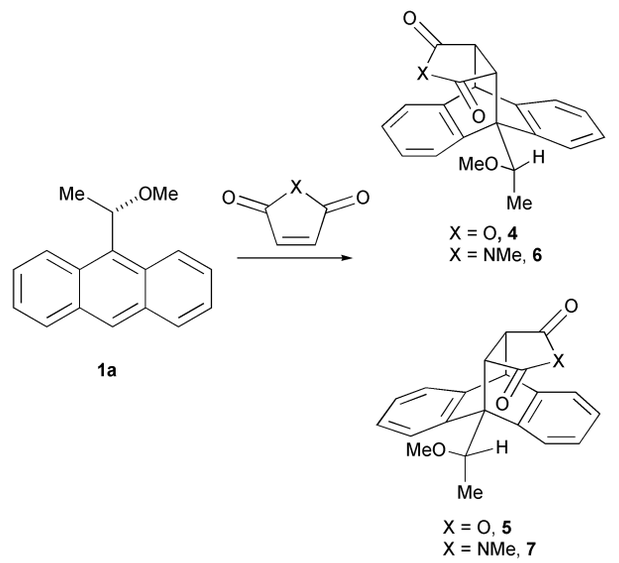
Thermal Diels–Alder reactions

The thermal Diels–Alder addition of maleic anhydride and *N*-methylmaleimide with the auxiliary **1a** was first performed by heating at reflux in degassed toluene for 3 hours, providing exclusively the addition products **5** and **7** as single diastereoisomers respectively (Scheme 3). The relative stereochemistry of the addition products **5** and **7** was confirmed by single crystal X-ray diffraction which clearly shows the orientation of the methoxy group away from the carbonyl group with the methyl antiperiplanar to the ring system (Fig. 2).

Table 1 Thermal Diels–Alder additions of ether **1a** with maleic anhydride (X = O) and *N*-methylmaleimide (X = NMe)

		Conversion (%)[a]		
	Time/min	Toluene	Xylene	Mesitylene
X = O	30	62	85	90
	60	77	92	91
	120	91	96	90
X = NMe	30	86	92	94
	60	91	95	95
	120	96	97	95

[a] Ratios calculated by integration of the signals corresponding to starting material **1a** and addition product **5** or **7** in the ^{1}H NMR spectrum.



Scheme 3

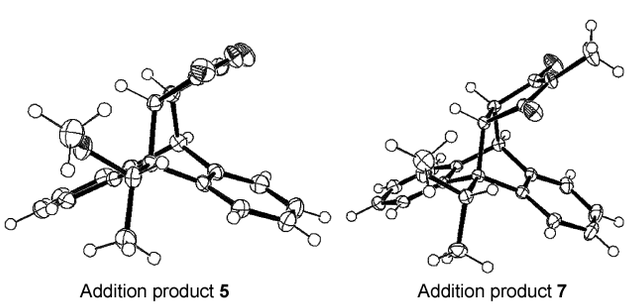


Fig. 2

Further studies were carried out to optimise the thermal addition process and provide a simple comparision of the relative reaction rate of the ether **1a** and the two dienophiles by heating at reflux in a dry degassed solvent for two hours and sampling each reaction at time intervals. The ratio of starting material to product was determined by integration of the appropriate signals in the ^{1}H NMR spectrum and the results are shown in Table 1, Figure 4 and Figure 5.

In each case essentially a single diastereoisomer was obtained from all of the reactions, although a slight reduction in diastereoselectivity to approximately 95 : 5 was observed when mesitylene was used as solvent. Increasing the reflux temperature by changing solvent from toluene (111 °C) to mixed xylenes (137–144 °C) increased the rate of the reaction and the amount of product obtained. Similar results were obtained by a further increase in reflux temperature by changing to mesitylene (162–164 °C) giving higher yield of products **5** and **7**. The rate of addition of *N*-methylmaleimide was found to be significantly faster than with maleic anhydride which is somewhat surprising since the [4 + 2]cycloaddition of

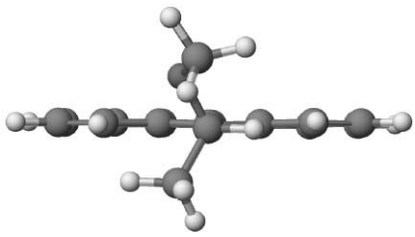


Fig. 3 Stable conformer of ether **1a**.

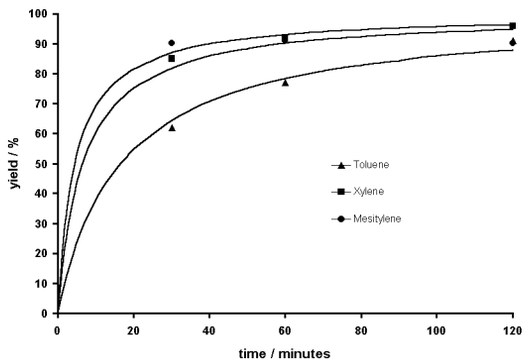


Fig. 4 Kinetics of the thermal Diels–Alder addition of ether **1a** with maleic anhydride.

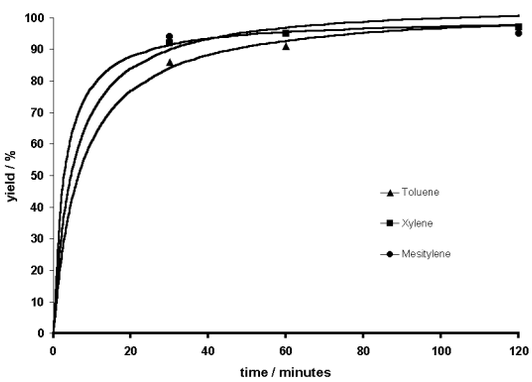


Fig. 5 Kinetics of the thermal Diels–Alder addition of ether **1a** with *N*-methylmaleimide.

trans,trans-1,4-diphenylbuta-1,3-diene with maleic anhydride is 3 times *faster* than with *N*-methylmaleimide in toluene at 110 °C.[12] The latter is what would be predicted, since maleic anhydride would be expected to be a more electron deficient dienophile than *N*-methylmaleimide. This effect appears to be characteristic of anthryl dienes since similar rate profiles to those shown in Fig. 4 and Fig. 5 can be obtained when employing anthracene itself as the diene, although such reactions are somewhat slower than those with ether **1a**. No evidence could be obtained for the existence of an intermediate charge-transfer complex that could account for an increase in reaction rate of the maleimide addition.[13] A possible explanation is that the rate of the competing retro Diels–Alder reaction of adduct **5** is greater than that with the adduct with *N*-methylmaleimide, **7**, resulting in an overall reduced reaction rate. The apparent anomolous reactivity difference compared to the predicted and observed reaction rates with *trans,trans*-1,4-diphenylbuta-1,3-diene is due to the retro Diels–Alder reaction of this compound being less facile than with the anthracene adducts. Exchange reactions between anthracene Diels–Alder products and butadiene have been observed that support this hypothesis.[14]

Previous studies of related Diels–Alder additions proposed by Sanyal and Snyder[7] and for singlet oxygen additions by Adam *et al.*[15] have rationalised the selectivity based upon kinetic control. Although it is tempting to apply such a model to this system, it does not fully explain the anomalous reaction rates with anhydride and maleimide dienophiles, nor account for the unchanged selectivity at elevated temperatures. An explanation based upon the thermodynamic stability of the diastereoisomers is more satisfactory, although the transition states and respective products in these reactions would be very similar. Molecular modelling studies (Fig. 3) of the the ground state conformation of ether **1a** have indicated that the anthracyl ring bisects the Me and OMe groups in order to minimise *peri* interactions of these groups with the H-1 and H-8 protons. This is evident in a predicted restricted rotation about the C-9 bond with an energy barrier of 9.3 kcal mol^{-1}. Broadened signals for the protons at H-1 and H-8 are indeed observed in the ^{1}H NMR spectrum and the measured energy for the rotation about the C-9 bond was found to be 12.2 kcal mol^{-1} at 281 K which is in good agreement with the calculated value. Of the two diastereoisomers that are possible from addition of a dienophile to ether **1a**, the isomer with the carbonyl group orientated away from the methoxy group is favored as steric and electronic repulsion between the respective oxygen atoms is minimised. Predicted equilibrium constants for the two diastereoisomers obtained from their calculated heats of formation provide support for this argument (Table 2).

Table 2 Predicted ΔH_f and calculated and observed equilibrium constants for the diastereoisomers obtained from the Diels–Alder additions of ether **1a** with maleic anhydride and *N*-methylmaleimide

Compound	ΔH_f	Calculated K_{eq} [a]	Observed dr
4	−93.63		
5	−98.47	1.9×10^{-3}	> 95 : 5
6	−52.85		
7	−58.59	0.58×10^{-3}	> 95 : 5

[a] Obtained from the calculated energy differences at 110 °C.

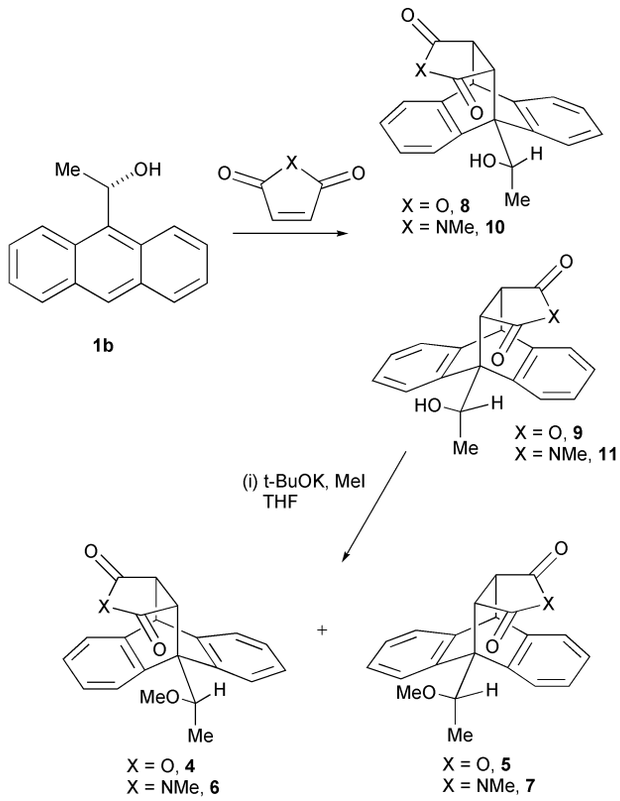
Table 3 Thermal Diels–Alder additions of alcohol **1b** with maleic anhydride (X = O) and *N*-methylmaleimide (X = NMe)

		Conversion (%) [a]		
	Time/min	Toluene	Xylene	Mesitylene
X = O	30	91	92	98
	60	95	97	99
	120	99	98	99
X = NMe	30	100	100	100
	60	100	100	100
	120	100	100	100

[a] Ratios calculated by integration of the signals corresponding to starting material **1b** and addition products **8**, **9** or **10**, **11** in the ^{1}H NMR spectrum.

Similar simple kinetic studies were carried out with the anthryl carbinol **1b** with the same range of substrates (Scheme 4). However, in this case formation of two diastereomeric products were observed in a ratio of approximately 75 : 25 with maleic anhydride and 55 : 45 with *N*-methylmaleimide. It was also noted that the reactions were significantly faster than with the ether **1a** in the same solvents (Table 3, Fig. 6, Fig. 7). Separation of the diastereoisomers **8** and **9** proved difficult, although sufficient quantities of each were collected to facilitate characterisation. However diastereosimers **10** and **11** could not be separated. The identity of the respective diastereoisomers was confirmed by methylation of the more readily available minor isomer **9** and a mixture of isomers **10** and **11** using *t*-BuOK and methyl iodide.† Use of sodium hydride for this methylation failed to give any product, returning unreacted starting

† Identical results were obtained when methylation was performed on mixtures of **10** and **11** containing a greater proportion of **11** obtained from photochemical experiments (see later).



Scheme 4

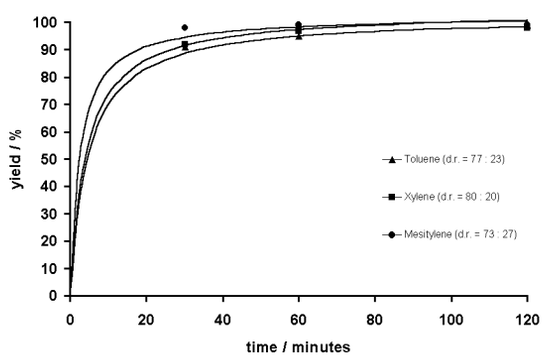


Fig. 6 Kinetics of the thermal Diels–Alder additions of carbinol **1b** with maleic anhydride.

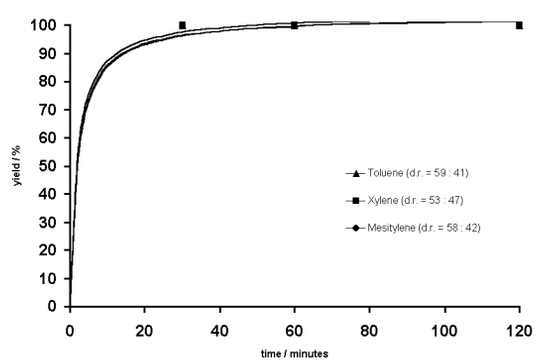


Fig. 7 Kinetics of the thermal Diels–Alder additions of carbinol **1b** with *N*-methylmaleimide.

material. From correlation of the methyl ethers obtained it was deduced that the major diastereoisomer **8** obtained from the reaction of maleic anhydride with substrate **1b** possessed the opposite sense of diastereoselectivity to that with substrate **1a**. However, with *N*-methylmaleimide the major diastereoisomer was surprisingly the addition product **11** with the same sense of diastereoselectivity observed with the methyl ether **1a**.

Table 4 Predicted ΔH_f and calculated and observed equilibrium constants for the diastereoisomers obtained from the Diels–Alder additions of alcohol **1b** with maleic anhydride and *N*-methylmaleimide.

Compound	ΔH_f	Calculated K_{eq} [a]	Observed dr
8	−103.48	0.26	75 : 25
9	−104.51		
10	−63.74	0.34	55 : 45
11	−64.58		

[a] Obtained from the calculated energy differences at 110 °C.

These apparently inconsistent reversals in the diastereoselectivity coupled with the increase in rate can be explained by considering the presence of hydrogen bonding in the products. Molecular modelling studies again confirmed that the preferred conformation of the alcohol was analogous to the ether **1a** with a calculated rotational energy barrier of 9.7 kcal mol^{-1}, again comparing well to the calculated (10.92 kcal mol^{-1} MM2) and the observed (11.0 kcal mol^{-1} at 245 K) literature values.[16] In an analogous fashion to additions with the ether **1a**, electrostatic repulsion of the carbonyl oxygen atom and the hydroxy group favor **9** or **11**, however, formation of a hydrogen bond would stabilise the other diastereoisomer and in-part override the electrostatic repulsion favoring diastereomer **8** or **10**. The loss of the sterically demanding methyl group and the introduction of a hydrogen bond also now result in the products from this reaction being more stable than those with the ether **1a**. This in turn would lead to a decrease in the rate of the retro Diels–Alder addition and hence an overall apparent acceleration in reaction rate. We have previously reported evidence for such a hydrogen bond based upon molecular modelling of the transition state of this reaction.[6] However, direct experimental evidence for this hypothesis was difficult to determine using *in situ* ^{1}H NMR and IR measurements of the reactions. Once again, predicted equilibrium constants of the diastereomeric addition adducts agree reasonably well with the observed selectivities (Table 4).

In the case of *N*-methylmaleimide additions, the same effects operate, except that an additional factor must be present that now increases the electrostatic interaction between the carbonyl oxygen and the alcohol providing more of the diastereosiomer with the carbonyl and hydroxy group orientated away from each other. Although the basis for this additional effect is not yet clear, it is reasonable to assume that it lies in the extra steric bulk provided by the *N*-methyl group. Further work to elucidate this hypothesis is currently underway.

Photoinduced Diels–Alder reactions

The photoinduced Diels–Alder reaction of substrate **1a** with maleic anhydride and *N*-methylmaleimide were performed using a semi-micro photochemical reactor with a 2 W source at 254 nm in a variety of solvents. The reactions were halted after three hours and the ratio of starting material to product calculated from integration of the signals in the ^{1}H NMR spectrum (Table 5). The results once again demonstrate the high levels of diastereoselectivity in this reaction, returning a single diastereoisomer **5** and **7** in each case with the same sense of diastereoselection as noted for the thermal additions. A similar trend was also observed as with the thermal additions in the increased conversion obtained when using *N*-methylmaleimide as a dienophile. The temperature of the reactor was monitored during the course of this reaction and found to reach a maximum of approximately 40 °C after 1 hour. Thus control reactions carried out in the dark at 30 °C showed that in some cases the reaction rate was indeed accelerated by use of photochemical conditions. Illumination at 254 nm for longer reaction times afforded quantitative conversion to the addition products **5** and **7**. It should be noted that the reagents were only

Table 5 Photoinduced Diels–Alder additions of ether **1a** with maleic anhydride (X = O) and *N*-methylmaleimide (X = NMe) including control reactions

	Conversion/%[a]					
	THF	CH_3CN	Et_2O	$PhCH_3$	C_7H_{16}[d]	CH_2Cl_2
X = O						
Photoinduced[b]	9	23	26	30	33	54
Control[c]	6	22	13	29	18	39
X = NMe						
Photoinduced[b]	80	67	77	72	89	91
Control[c]	54	68	81	73	79	84

[a] Ratios calculated by integration of the signals corresponding to starting material **1a** and addition products **5** or **7** in the ^{1}H NMR spectrum. [b] Illuminated at 254 nm in 4 cm^3 degassed solvent under a nitrogen atmosphere for 3 h. [c] Heated at 30 °C in the dark in 4 cm^3 degassed solvent under a nitrogen atmosphere for 3 h. [d] Reagents were only partially soluble in heptane.

Table 6 Photoinduced Diels–Alder additions of ether **1b** with maleic anhydride (X = O) and *N*-methylmaleimide (X = NMe) including control reactions.

	Conversion/%[a]					
	THF	CH_3CN	Et_2O	$PhCH_3$	C_7H_{16}[d]	CH_2Cl_2
X = O						
Photoinduced[b]	38 (93 : 7)	47 (89 : 11)	73 (90 : 10)	76 (82 : 18)	47 (86 : 14)	100 (81 : 19)
Control[c]	16 (95 : 5)	30 (90 : 10)	43 (92 : 8)	65 (84 : 16)	39 (82 : 12)	90 (82 : 18)
X = NMe						
Photoinduced[b]	100 (80 : 20)	100 (66 : 34)	81 (70 : 30)	100 (56 : 44)	100 (58 : 42)	100 (50 : 50)
Control[c]	100 (78 : 22)	100 (70 : 30)	100 (74 : 26)	100 (54 : 46)	100 (50 : 50)	100 (51 : 49)

[a] Ratios calculated by integration of the signals corresponding to starting material **1b** and addition products **8**, **9** and **11**, **10** in the ^{1}H NMR spectrum. Diastereomeric ratios for the addition products **8** : **9** and **11** : **10** respectively are given in parentheses. [b] Illuminated at 254 nm in 4 cm^3 degassed solvent under a nitrogen atmosphere for 3 h. [c] Heated at 30 °C in the dark in 4 cm^3 degassed solvent under a nitrogen atmosphere for 3 h. [d] Reagents were only partially soluble in heptane.

partially soluble in heptane, limiting the use of this solvent for comparison of reaction rates.

There are several interesting solvent effects observed in these photoinduced and control reactions. For maleic anhydride additions with anthracene derivatives **1a** and **1b**, a general solvent dependancy of the reactivity is observed in the order CH_2Cl_2 > $PhCH_3$ > Et_2O > CHCN > THF, the only exception being a reversal in reactivity of control reactions of **1a** in CH_3CN and Et_2O (Table 6). This order broadly follows that reported for the addition of other dienophiles to anthracene derivatives.[17] Once again a substantial difference in the reaction rate between additions carried out with *N*-methylmaleimide and maleic anhydride was observed, as was a general increase in reaction rate for additions carried out with the alcohol **1b** compared to the ether **1a**. These observations can again be explained using the arguments presented earlier.

Most interestingly amongst these results are the differences in the diastereoselectivities observed with additions to the carbinol **1b** in different solvents. There appears to be general divide with the solvents $PhCH_3$, C_7H_{16} and CH_2Cl_2 giving lower selectivities than those in THF, CH_3CN and Et_2O, an effect that is more pronounced with additions involving *N*-methylmaleimide than with maleic anhyride. In the former, higher selectivities are generally observed in those solvents with a hydrogen-bond acceptor bascitiy term $\beta \geq 0.31$[18] where the hydroxy group can preferentially form hydrogen bonds to the solvent rather than the carbonyl group. This helps negate the stability of the addition product afforded by the hydrogen bonding, returning the control of stereoselecitivity to electrostatic repulsion of the oxygen atoms. In each case, the increase in the ratio of addition adduct **11** observed follows an increase in the experimentally derived β parameters for these solvents. With additions involving maleic anhydride, the variation in selectivity observed is much less, indicating that hydrogen bonding plays a much more important role that is less dependant upon solvent effects than in those with *N*-methylmaleimide. Attempts at providing further experimental confirmation of these results by using hydrogen bond acceptor solvents such as methanol or ethanol were unsuccessful due to poor solubility of the anthracene derivatives **1a**, **1b** in such solvents.

Conclusions

We have investigated the efficiency and selectivity of cycloadditions of maleic anhydride and *N*-methylmaleimide to two anthracene substrates **1a** and **1b**. The origins of the stereoselectivity in these reactions[7] were consistent with models proposed by Sanyal and Snyder and by us.[6] Solvent effects on the observed diastereoselectivity have provided tentative evidence for existance of a hydrogen bond. We are in the process of examining the reactions of other dienophiles such as methyl vinyl ketone and benzoquinone under both thermal and photochemical conditions and also conducting a more detailed study of the photochemistry of this reaction and the retro-Diels–Alder reaction.

Experimental

All solvents used were freshly dried over sodium (except dichloromethane which was dried over lithium aluminium hydride). Glassware was flame dried and cooled under vacuum before use. All reactions were carried out under nitrogen. TLC was carried out using Merck aluminium TLC sheets (silica gel 60 F_{254}). Visualisation of the TLC plates was carried out using a UV lamp or by dipping in $KMnO_4$ or $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ then exposure by heating. Flash column chromatography was carried out with Fluorochem Limited Silica Gel 40–63u 60A. 200 MHz ^{1}H NMR were carried out on a Bruker AC200

spectrometer using the Bruker Aspect 3000 system. 300 MHz ^{1}H NMR were carried out on a Bruker Avance 300 spectrometer. 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR were carried out on JEOL (Japan Electron Optical Limited) Lamda 500 MHz spectrometer. Residual proton signals from the deuteriated solvents were used as references [chloroform (^{1}H 7.25 ppm, ^{13}C 77 ppm) and DMSO (^{1}H 2.50 ppm, ^{13}C 39.7 ppm)]. Coupling constants were measured in Hz. Specific rotations were performed on a Polaar 2001 automatic polarimeter at 589 nm and measured at 20 °C unless otherwise stated. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. All infrared spectra were recorded on a Nicolet 5-PC FT-IR spectrophotometer and mass spectra were recorded on a Micromass Autospec M spectrometer. HPLC was carried out using a Spectra Physics Analytical system (consisting of a P4000 pump, a AS1000 autosampler, a UV2000 detector and using PC 1000 version 2.0 software). A Chiralcel OD (4.8 mm × 250 mm) column was used with 10% IPA in heptane as the solvent (unless otherwise stated). The flow rate was 1.00 cm^3 per minute and the detector was set at 254 nm.

1-Anthracen-9-ylethanone 3

A solution of anthracene **2** (5.0 g, 28.0 mmol) and acetyl chloride (12.0 cm^3, 168.3 mmol) in dry dichloromethane (100 cm^3) was cooled to −5 °C in an ice–calcium chloride bath. Aluminium chloride (7.48 g, 56.1 mmol) was added slowly with vigorous stirring maintaining the temperature between −5 and 0 °C. The resulting solution was stirred for 30 min at −5 °C and then warmed slowly to 10 °C. The red solution was poured into a beaker containing ice and concentrated HCl. Once the ice had melted, the product was extracted into dichloromethane, washed with water (3 × 20 cm^3) and dried over $MgSO_4$. Filtration and removal of the solvent yielded a lustrous red oil which solidified on standing (6.28 g). The crude product was dissolved in hot ethanol (60 cm^3), heated at reflux for 30 min then cooled rapidly to near room temperature. The solution was filtered (to remove any precipitate of anthracene) then heated again. Slow cooling produced light orange–brown crystals of the title compound which were filtered and dried *in vacuo* (4.49 g, 20.4 mmol, 73%); mp 75–76 °C (from EtOH) (lit.,[8] 75–76 °C from EtOH–H_2O); δ_H (200 MHz; $CDCl_3$) 2.84 (3 H, s, C*H*$_3$), 7.50–7.58 (4 H, m, Ph), 7.87 (2 H, m, Ph), 8.06 (2 H, m, Ph), 8.52 (1 H, s, Ph); δ_C (125 MHz; $CDCl_3$) 33.8 (*C*H$_3$), 124.3 (2 × Ar*C*H), 125.5 (2 × Ar*C*H), 126.6 (2 × Ar*C*), 126.7 (2 × Ar*C*H), 128.2 (Ar*C*H), 128.8 (2 × Ar*C*H), 131.0 (2 × Ar*C*), 136.7 (Ar*C*), 208.1 (*C*=O).

(±)-1-Anthracen-9-ylethanol 1b

Sodium borohydride (0.26 g, 6.82 mmol) was added to a stirred solution of 1-anthracen-9-ylethanone **3** (1.00 g, 4.5 mmol) in ethanol (50 cm^3). The solution was heated at reflux for 2.5 h and then allowed to cool to room temperature. Aqueous ammonium chloride (10 cm^3) was added and the product was extracted into dichloromethane (3 × 10 cm^3), which was then dried over $MgSO_4$. Removal of the solvent gave the title compound **1b** as an orange–yellow solid (1.00 g, 4.51 mmol, 100%) which could be used in subsequent reactions without purification; mp 119–120 °C (lit.,[7] 121–122 °C from Et_2O); δ_H (200 MHz; $CDCl_3$) 1.95 (3 H, d, *J* 6.8, C*H*$_3$), 2.27 (1 H, br s, O*H*), 6.50 (1 H, q, *J* 6.8, CH$_3$C*H*), 7.28–7.60 (4 H, m, Ph), 7.92 (2 H, m, Ph), 8.32 (1 H, s, 10-H), 8.70 (2 H, br d, *J* 9.3, H-4, H-5); δ_C (125 MHz; $CDCl_3$) 23.4 (*C*H$_3$), 67.2 (CH$_3$*C*H), 124.7 (4 × Ar*C*H), 125.4 (2 × Ar*C*H), 127.9 (Ar*C*H), 128.7 (2 × Ar*C*), 129.3 (2 × Ar*C*H), 131.6 (2 × Ar*C*), 135.7 (Ar*C*).

(±)-9-(1-Methoxyethyl)anthracene 1a

Sodium hydride (0.90 g, 22.6 mmol) was washed with petrol then dried *in vacuo* for 30 min. THF (60 cm^3) was added and the stirred solution cooled to 0 °C. A solution of 1-anthracen-9-ylethanol **1b** (3.34 g, 15.0 mmol) in dry THF (15 cm^3) was added dropwise *via* cannula. The resulting solution was allowed to warm to room temperature and stirred for 2 h. Methyl iodide (1.1 cm^3, 18.0 mmol) was added and the solution stirred for a further 22 h. After cooling to 0 °C, methanol (20 cm^3) was added dropwise followed by water (20 cm^3). The resulting solution was separated and extraction carried out with ethyl acetate (3 × 20 cm^3), which was combined with the organic layer and dried over $MgSO_4$. The solvent was then removed to leave a brown solid (4.61 g). Flash column chromatography (50% dichloromethane in petrol), followed by recrystallisation from ethanol yielded the title compound **1a** as golden crystals (2.24 g, 9.5 mmol, 63%); mp 89–91 °C (from EtOH) (lit.,[7] 78–79 °C from CH_2Cl_2-hexane); δ_H (200 MHz; $CDCl_3$) 1.88 (3 H, d, *J* 6.8, C*H*$_3$), 3.23 (3 H, s, OC*H*$_3$), 5.95 (1 H, q, *J* 6.8, CH$_3$C*H*), 7.44–7.56 (4 H, m, Ph), 8.02 (2 H, m, Ph), 8.43 (1 H, s, 10-H), 8.71 (2 H, br s, 4-H, 5-H); δ_C (125 MHz; $CDCl_3$) 22.5 (*C*H$_3$), 56.5 (O*C*H$_3$), 76.1 (CH$_3$*C*H), 124.4 (2 × Ar*C*H), 124.8 (2 × Ar*C*H), 125.5 (2 × Ar*C*H), 127.8 (Ar*C*H), 129.3 (2 × Ar*C*H), 129.5 (2 × Ar*C*), 131.6 (2 × Ar*C*), 133.4 (Ar*C*).

(*S*)-1-Anthracen-9-ylethanol 1b

Trimethylboroxine (0.19 cm^3, 1.34 mmol) was added to a solution of (1*R*, 2*S*)-1-aminoindan-2-ol (0.30 g, 2.01 mmol) in dry toluene (10 cm^3) and stirred at room temperature for 30 min. Toluene (10 cm^3) was added and the resulting solution was concentrated to approximately 2 cm^3 by distillation. This process was repeated twice after which the toluene was removed *in vacuo* to give the catalyst as a white solid. THF (2 cm^2) was added to produce an approximately 1 M solution of catalyst in THF that was used in subsequent reactions.

BH_3·THF (1 M, 2.50 cm^3, 2.50 mmol) was added to a solution of the above catalyst (0.23 cm^3, 0.23 mmol) in dry THF (1.20 cm^3) and stirred at room temperature under nitrogen for 30 min. The resulting solution was cooled to 0 °C and 1-anthracen-9-ylethanone **3** (0.50 g, 2.27 mmol) in dry THF (2.5 cm^3) added *via* syringe pump (0.0132 cm^3 min^{-1}). The reaction mixture was stirred overnight at 0 °C (gradually warmed to room temperature) then quenched with methanol (10 cm^3, at 0 °C) and allowed to warm to room temperature for 10 min. Water (10 cm^3) was added and the organic solvent removed under reduced pressure. The product was extracted into dichloromethane (3 × 10 cm^3), the organic phase washed with 1 M HCl (10 cm^3), water (10 cm^3) and dried over $MgSO_4$. Removal of the solvent *in vacuo* produced the title compound (*S*)-**1b** as a yellow solid (0.48 g, 2.17 mmol, 95%); mp 116–117 °C (from EtOH) (lit.,[19] 121–122 °C from CH_2Cl_2–petrol 40–60); $[\alpha]_D$ −17.5 (*c* 1, $CHCl_3$ ee 96%) (lit.,[19] $[\alpha]_D$ –18.8 (*c* 1.1, $CHCl_3$ ee > 99%); δ_H (200 MHz; $CDCl_3$) 1.78 (3 H, d, *J* 6.8, C*H*$_3$), 2.17 (1 H, br s, O*H*), 6.34 (1 H, q, *J* 6.8, CH$_3$C*H*), 7.18–7.50 (4 H, m, Ph), 7.92 (2 H, m, Ph), 8.22 (1 H, s, 10-H), 8.60 (2 H, br d, *J* 9.3, 4-H, 5-H); δ_C (125 MHz; $CDCl_3$) 23.4 (*C*H$_3$), 67.1 (CH$_3$*C*H), 124.7 (4 × Ar*C*H), 125.4 (2 × Ar*C*H), 127.9 (2 × Ar*C*H), 128.7 (2 × Ar*C*), 129.2 (2 × Ar*C*), 131.6 (Ar*C*H), 135.7 (Ar*C*).

(*S*)-9-(1-Methoxyethyl)anthracene 1a

From (*S*)-1-anthracen-9-ylethanol **1b** (0.200 g, 0.90 mmol), the title compound was prepared as for (±)-9-(1-methoxyethyl)-anthracene **1a** as golden crystals (0.189 g, 0.80 mmol, 89%); mp 99–100 °C (from EtOH); $[\alpha]_D$ −44.6 (*c* 1, $CHCl_3$ ee 96%); δ_H (300 MHz; $CDCl_3$) 1.88 (3 H, d, *J* 6.8, C*H*$_3$), 3.24 (3 H, s, OC*H*$_3$), 5.96 (1 H, q, *J* 6.8, CH$_3$C*H*), 7.46–7.55 (4 H, m, Ph), 8.03 (2 H, m, Ph), 8.43 (1 H, s, 10-H), 8.70 (2 H, br s, 4-H, 5-H); δ_C (125 MHz; $CDCl_3$) 22.5 (*C*H$_3$), 56.5 (O*C*H$_3$), 76.1 (CH$_3$*C*H), 124.4 (2 × Ar*C*H), 124.8 (2 × Ar*C*H), 125.5 (2 × Ar*C*H), 127.8 (Ar*C*H), 129.3 (2 × Ar*C*H), 129.5 (2 × Ar*C*), 131.6 (2 × Ar*C*), 133.4 (Ar*C*); *m*/*z* (EI) 236.1192 (M^+, $C_{17}H_{16}O$ requires 236.1201), 221 (100%), 206 (14) and 178 (32).

General procedure for the thermal additions of compounds 1a or 1b to maleic anhydride or *N*-methylmaleimide

A solution of anthryl derivative **1a** or **1b** (0.42 mmol) and dienophile (0.42 mmol) in dry degassed solvent (10 cm^3) was heated at reflux and sampled as appropriate. Removal of the solvent produced the desired cycloadduct.

General procedure for photoinduced Diels–Alder addition of compounds 1a and 1b to maleic anhydride or *N*-methylmaleimide

A solution of anthryl derivative **1a** or **1b** (0.21 mmol) and dienophile (0.26 mmol) in dry degassed solvent (4 cm^3) was irradiated in a quartz vessel at 254 nm. Samples were removed as appropriate. Water (10 cm^3) and dichloromethane (5 cm^3) were added and the organic phase separated and washed with water (2 × 10 cm^3) then dried (Na_2SO_4). Removal of the solvent produced unreacted anthryl derivative **1a** or **1b** and the desired cycloadduct (conversion calculated from ^{1}H NMR).

General control procedure for control Diels–Alder addition of compounds 1a and 1b to maleic anhydride or *N*-methylmaleimide

A solution of anthryl compound **1a** or **1b** (0.21 mmol) and dienophile (0.26 mmol) in dry degassed solvent (4 cm^3) was warmed at 30 °C for 3 h. Samples were removed as appropriate. Water (10 cm^3) and dichloromethane (5 cm^3) were added and the organic phase separated and washed with water (2 × 10 cm^3) then dried (Na_2SO_4). Removal of the solvent produced unreacted anthryl compound **1a** or **1b** and the desired cycloadduct (conversion calculated from ^{1}H NMR).

(11*S*,15*S*)-9,10,11,15-Tetrahydro-9-[(1*S*)-1-methoxyethyl]-9,10-[3′,4′]furanoanthracene-12,14-dione 5

Obtained in 47% isolated yield using the general procedure by heating with maleic anhydride in toluene for 4 h; mp 243–244 °C (from CH_2Cl_2–petrol 60–80) [lit.[7] (racemic) 242–243 °C, from CH_2Cl_2–hexane]; $[\alpha]_D$ +50.9 (*c* 1, $CHCl_3$ ee 96%); δ_H (300 MHz; $CDCl_3$) 1.91 (3 H, d, *J* 6.3, C*H*$_3$), 3.46 [1 H, dd, *J* 3.3 and 9.3, CHC*H*(C=O)], 3.72 (3 H, s, OC*H*$_3$), 3.97 [1 H, d, *J* 9.3, CH(C=O)C*H*(C=O)], 4.78 [1 H, d, *J* 3.3, C*H*CH(C=O)], 5.03 (1 H, q, *J* 6.3, CH$_3$C*H*), 7.19–7.30 (5 H, m, Ph), 7.39 (2 H, m, Ph), 7.88 (1 H, m, Ph); δ_C (125 MHz; $CDCl_3$) 16.6 (*C*H$_3$), 46.3 [(C=O)CH], 48.2 [(C=O)CH], 49.5 (10-C), 54.5 (9-C), 57.2 (O*C*H$_3$) 73.4 (CH$_3$*C*H), 123.8 (Ar*C*H), 124.0 (Ar*C*H), 125.4 (Ar*C*H), 126.3 (Ar*C*H), 126.7 (Ar*C*H), 126.9 (Ar*C*H), 127.4 (Ar*C*H), 127.5 (Ar*C*H), 137.9 (Ar*C*), 138.3 (Ar*C*), 138.5 (Ar*C*), 141.7 (Ar*C*), 169.4 (*C*=O), 170.6 (*C*=O); *m*/*z* (EI) 334.1218 (M^+ $C_{21}H_{18}O_4$ requires 334.1205), 236 (100%), 221 (81), 205 (15) and 178 (16).

(3a*S*,9a*S*)-3a,4,9,9a-Tetrahydro-4-[(1*S*)-1-methoxyethyl]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3-(2*H*)-dione 7

Obtained in 41% yield using the general procedure by heating with *N*-methylmaleimide in toluene for 4 h.; mp 206–208 °C (from CH_2Cl_2–petrol 60–80) [lit.,[7] (racemic) 243–244 °C CH_2Cl_2–hexane]; (Found: C, 76.4; H, 6.1; N, 4.1. $C_{22}H_{21}NO_3$ requires C, 76.1; H, 6.1; N, 4.0%); $[\alpha]_d$ +70.5 (*c* 0.5, $CHCl_3$ ee 96%); δ_H (300 MHz; $CDCl_3$) 1.88 (3 H, d, *J* 6.4, C*H*$_3$), 2.48 (3 H, s, NC*H*$_3$), 3.14 [1 H, dd, *J* 3.2 and 8.4, CHC*H*(C=O)], 3.63 [1 H, d, *J* 8.4, CH(C=O)C*H*(C=O)], 3.74 (3 H, s, OCH$_3$), 4.74 [1 H, d, *J* 3.2, C*H*CH(C=O)], 5.14 (1 H, q, *J* 6.4, CH$_3$C*H*), 7.13–7.24 (5 H, m, Ph), 7.31 (1 H, m, Ph), 7.40 (1 H, m, Ph), 7.90 (1 H, m, Ph); δ_C (125 MHz; $CDCl_3$) 16.7 (*C*H$_3$), 24.1 (N*C*H$_3$), 46.4 [(C=O)CH], 47.0 [(C=O)CH], 48.8 (10-C), 54.6 (O*C*H$_3$), 57.1 (9-C), 73.8 (CH$_3$*C*H), 123.5 (Ar*C*H), 123.9 (Ar*C*H), 125.1 (Ar*C*H), 125.8 (Ar*C*H), 126.3 (Ar*C*H), 126.6 (Ar*C*H), 126.7 (Ar*C*H), 126.8 (Ar*C*H), 138.2 (Ar*C*), 138.8 (Ar*C*), 139.2 (Ar*C*), 142.3 (Ar*C*), 176.3 (*C*=O), 176.8 (*C*=O); *m*/*z* (EI) 347.1529 (M^+, $C_{22}H_{21}NO_3$ requires 347.1521), 332 (8%), 289 (1), 235 (100), 221 (94), 205 (15) and 178 (24).

(11*R*,15*R*)-9,10,11,15-Tetrahydro-9-[(1*S*)-1-hydroxyethyl]-9,10-[3′,4′]furanoanthracene-12,14-dione 8 and (11*S*,15*S*)-9,10,11,15-tetrahydro-9-[(1*S*)-1-hydroxyethyl]-9,10-[3′,4′]-furanoanthracene-12,14-dione 9

Obtained in 100% yield as a 74 : 26 ratio of **8** : **9** using general procedure A by heating with maleic anhydride in toluene for 3 h. Separation of the diastereoisomers was carried out by repeated flash column chromatography (0.5 cm^3 MeOH in 100 cm^3 CH_2Cl_2); *major diastereoisomer* **8**: mp 179–180 °C; (Found: C, 74.8; H, 5.2. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%); $[\alpha]_D$ +7.2 (*c* 1, $CHCl_3$ ee 96%); δ_H (300 MHz; DMSO) 1.81 (3 H, d, *J* 6.4, C*H*$_3$), 3.54 [1 H, dd, *J* 3.2 and 9.2, CHC*H*(C=O)], 3.92 [1 H, d, *J* 9.2, CH(C=O)C*H*(C=O)], 4.82 [1 H, d, *J* 3.2, C*H*CH(C=O)], 5.53 (1 H, m, CH$_3$C*H*), 5.71 (1 H, d, *J* 4.4, OH), 7.15–7.38 (6 H, m, Ph), 7.48 (1 H, m, Ph), 7.98 (1 H, m, Ph); δ_C (125 MHz; DMSO) 21.0 (*C*H$_3$), 45.2 [(C=O)*C*H], 48.6 [(C=O)*C*H], 49.6 (10-C), 53.5 (9-C), 62.9 (CH$_3$*C*H), 123.8 (Ar*C*H), 124.1 (Ar*C*H), 124.9 (Ar*C*H), 125.5 (Ar*C*H), 126.1 (Ar*C*H), 126.8 (2 × Ar*C*H), 126.9 (Ar*C*H), 138.8 (2 × Ar*C*), 139.2 (Ar*C*), 142.5 (Ar*C*), 169.9 (*C*=O), 171.4 (*C*=O); *m*/*z* (EI) 320.1044 (M^+ $C_{20}H_{16}O_4$ requires 320.1049), 222 (100%), 207 (39) and 179 (62); *minor diastereoisomer* **9**: mp 215–216 °C; $[\alpha]_D$ +14.6 (*c* 0.25, $CHCl_3$ ee 96%); δ_H (300 MHz; DMSO) 1.81 (3 H, d, *J* 6.6, C*H*$_3$CH), 3.55 [1 H, d, *J* 9.2, CH(C=O)C*H*-(C=O)], 3.71 [1 H, dd, *J* 3.4 and 9.2, CHC*H*(C=O)], 4.78 [1 H, d, *J* 3.4, C*H*CH(C=O)], 5.24 (1 H, m, CH$_3$C*H*), 5.53 (1 H, d, *J* 4.7, OH), 7.12–7.32 (5 H, m, Ph), 7.47 (1 H, m, Ph), 7.61 (1 H, d, *J* 7.3, Ph), 7.97 (1 H, m, Ph); δ_C (125 MHz; DMSO) 20.1 (*C*H$_3$), 44.6 [(C=O)CH], 49.0 [(C=O)CH], 49.4 (10-C), 51.7 (9-C), 64.3 (CH$_3$*C*H), 124.2 (Ar*C*H), 124.5 (Ar*C*H), 124.6 (Ar*C*H), 125.5 (Ar*C*H), 125.9 (Ar*C*H), 126.6 (Ar*C*H), 126.7 (2 × Ar*C*H), 139.3 (Ar*C*), 139.6 (Ar*C*), 140.9 (Ar*C*), 142.7 (Ar*C*), 170.3 (*C*=O), 171.4 (*C*=O); *m*/*z* (EI) 320.1035 (M^+ $C_{20}H_{16}O_4$ requires 320.1049), 222 (100%), 207 (45) and 179 (77).

(11*S*,15*S*)-9,10,11,15-Tetrahydro-9-[(1*S*)-1-methoxyethyl]-9,10-[3′,4′]furanoanthracene-12,14-dione 5

A solution of the minor diastereoisomer **9** (0.17 g, 0.49 mmol) in dry THF (20 cm^3) was added *via* cannula to a solution of *t*-BuOK (0.07 g, 0.59 mmol) in dry THF (14 cm^3) at 0 °C. The resulting orange solution was allowed to warm to room temperature and stirred for 4 h. Methyl iodide (0.12 cm^3, 1.45 mmol) was added and the reaction left to stir overnight. Water (20 cm^3) was added and the product extracted into ethyl acetate (3 × 10 cm^3), dried over Na_2SO_4, filtered and the solvent removed to leave a light brown oily solid. Repeated flash column chromatography (ethyl acetate–petrol, 1 : 4) yielded compound **5** as a white solid with an identical ^{1}H NMR spectrum to that prepared earlier.

(3a*S*,9a*S*)-3a,4,9,9a-Tetrahydro-4-[(1*S*)-1-hydroxyethyl]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione 11 and (3a*R*,9a*R*)-3a,4,9,9a-tetrahydro-4-[(1*S*)-1-hydroxyethyl]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione 10

Obtained in quantitative yield as a 51 : 49 ratio of **11** : **10** using the general procedure by heating with *N*-methylmaleimide in toluene for 3 h. The diastereoisomers were inseparable by column chromatography and were characterised as a mixture; mp 93–94 °C; $[\alpha]_D$ +6.75 (*c* 1, $CHCl_3$ ee 96%); δ_H (300MHz; DMSO) *major diastereoisomer* 1.77 (3 H, d, *J* 6.0, C*H*$_3$), 2.30 (3 H, s, NC*H*$_3$), 3.14 [1 H, dd, *J* 3.1 and 8.3, CHC*H*(C=O)], 3.55 [1 H, d, *J* 8.3, CH(C=O)C*H*(C=O)], 4.69 [1 H, d, *J* 3.1, C*H*CH(C=O)], 5.45 (2 H, m, CH$_3$C*H* and O*H*), 7.11–7.25 (6 H, m, Ph), 7.46 (1 H, m, Ph), 7.98 (1 H, m, Ph); *minor diastereo-*

isomer 1.83 (3 H, d, *J* 6.0, C*H*$_3$), 2.34 (3 H, s, NC*H*$_3$), 3.21 [1 H, d, *J* 8.5, CH(C=O)C*H*(C=O)], 3.28 [1 H, dd, *J* 3.2 and 8.5, CHC*H*(C=O)], 4.66 [1 H, d, *J* 3.2, C*H*CH(C=O)], 5.34 (2 H, m, CH$_3$C*H* and O*H*), 7.06–7.20 (5 H, m, Ph), 7.45 (1 H, m, Ph), 7.53 (1 H, m, Ph), 7.97 (1 H, m, Ph); δ_C (125MHz; DMSO) *major diastereoisomer* 21.1 (*C*H$_3$), 23.7 (N*C*H$_3$) 45.4 [(C=O)-CH], 46.6 [(C=O)CH], 48.3 (10-C), 53.7 (9-C), 63.2 (CH$_3$*C*H), 123.6 (Ar*C*H), 123.8 (Ar*C*H), 124.6 (Ar*C*H), 125.2 (Ar*C*H), 125.8 (Ar*C*H), 126.2 (Ar*C*H), 126.3 (Ar*C*H), 126.8 (Ar*C*H), 138.9 (Ar*C*), 139.3 (Ar*C*), 139.6 (Ar*C*), 143.0 (Ar*C*), 175.7 (*C*=O), 176.4 (*C*=O); *minor diastereoisomer* 20.2 (*C*H$_3$), 23.8 (N*C*H$_3$) 44.7 [(C=O)CH], 47.1 [(C=O)CH], 48.0 (10-C), 52.0 (9-C), 64.5 (CH$_3$*C*H), 123.9 (Ar*C*H), 124.0 (Ar*C*H), 124.2 (Ar*C*H), 125.0 (Ar*C*H), 125.4 (Ar*C*H), 125.8 (Ar*C*H), 126.1 (Ar*C*H), 126.7 (Ar*C*H), 139.3 (Ar*C*), 140.4 (Ar*C*), 141.0 (Ar*C*), 143.3 (Ar*C*), 175.7 (*C*=O), 176.4 (*C*=O); *m*/*z* (EI) 333.1371 (M^+ $C_{21}H_{19}NO_3$ requires 333.1365), 289 (16%), 222 (100), 207 (46), 179 (82) and 113 (61).

(3a*S*,9a*S*)-3a,4,9,9a-Tetrahydro-4-[(1*S*)-1-methoxyethyl]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione 7 and (3a*R*,9a*R*)-3a,4,9,9a-tetrahydro-4-[(1*S*)-1-methoxyethyl]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione 7

A solution of a mixture of the two diastereoisomers **10** and **11** of ratio 20 : 80 respectively (0.85 g, 0.26 mmol) in dry THF (8 cm^3) was added *via* cannula to a solution of *t*-BuOK (0.04 g, 0.31 mmol) in dry THF (2 cm^3) at 0 °C. The resulting orange solution was allowed to warm to room temperature and stirred for 4 h. Methyl iodide (0.06 cm^3, 1.02 mmol) was added and the reaction left to stir overnight. Water (10 cm^3) was added and the product extracted into ethyl acetate (3 × 10 cm^3), dried over Na_2SO_4, filtered and the solvent removed to leave a light brown oily solid. A mixture of compounds **6** and **7** were obtained as white solid in a ratio 20 : 80 repectively. The major isomer **7** had an identical ^{1}H NMR spectrum to that prepared earlier.

Molecular modelling

All molecular modelling was performed using Quantum CAChe software (version 3.2, Oxford Molecular Ltd). Minimised structures were generated by first minimising using MM3 parameters, followed by PM3 parameters. Rotational energy barriers for compounds **5** and **7** were calculated from an energy map generated by minimisation of conformers from searching the dihedral angle in increments of 15°.

X-Ray Crystallography

Crystal data for **5**: $C_{21}H_{18}O_4$, M_r = 334.4, triclinic, space group $P\bar{1}$, a = 9.5923(8), b = 10.1129(8), c = 19.9661(9) Å, α = 112.886(2), β = 94.278(2), γ = 117.285(2), U = 828.41(12) Å^3, Z = 2, D_c = 1.389 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.095 mm^{-1}, T = 160 K. Of 5885 reflections measured (Bruker SMART CCD area detector diffractometer; θ < 25.0°), 2885 were unique (R_{int} = 0.0225). The structure was solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained isotropic H atoms; $R(F; F^2>2\sigma)$ = 0.0511, $R_w(F^2$, all data) = 0.1120, goodness-of-fit = 1.129 for 229 refined parameters. Largest difference map features +0.28 and −0.20 e Å^{-3}.

Crystal data for **7**: $C_{22}H_{21}NO_3$, M_r = 347.4, monoclinic, space group $P2_1/c$, a = 10.7625(7), b = 9.6850(6), c = 16.7021(11) Å, β = 93.067(2)°, U = 1738.45(19) Å^3, Z = 4, D_c = 1.327 g cm^{-3}, μ = 0.088 mm^{-1}, T = 160 K. Of 14775 reflections measured (θ < 28.8°), 4136 were unique (R_{int} = 0.0286). $R(F; F^2>2\sigma)$ = 0.0661, $R_w(F^2$, all data) = 0.1509, goodness-of-fit = 1.204 for 238 refined parameters. Largest difference map features +0.46 and −0.30 e Å^{-3}. Programs used were standard Bruker SMART (data collection), SAINT (integration) and SHELXTL (structure solution and refinement), together with local software.

CCDC reference numbers 189242 and 189243. See http://www.rsc.org/suppdata/p1/b2/b206523a/ for crystallographic files in .cif or other electronic format.

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