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Preparation and Cycloaddition Reactions of Novel Heterocyclic Mesomeric Betaines

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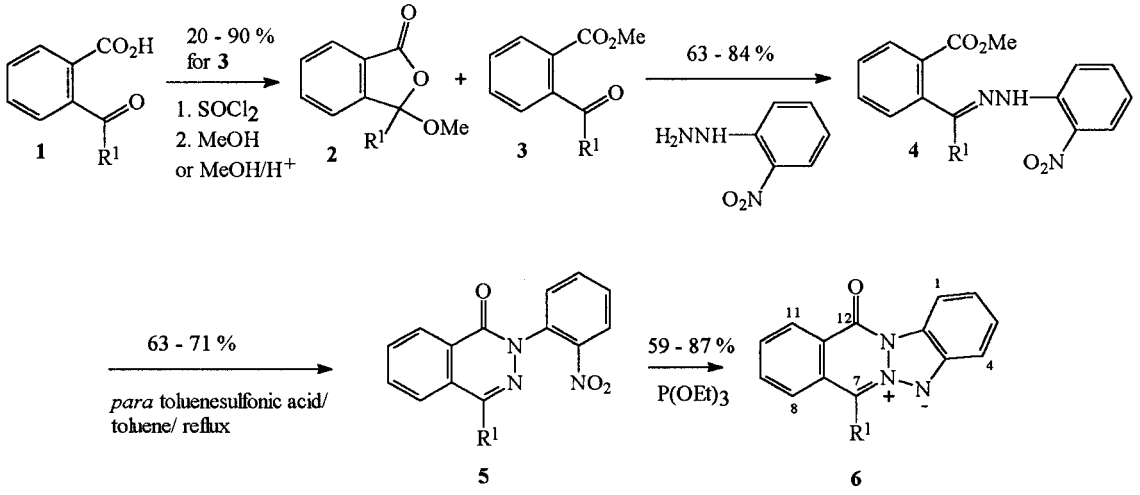
Abstract—The heterocyclic mesomeric betaines **6a–c** reacted with dimethyl acetylenedicarboxylate and ethyl propiolate giving the 1,3-dipolar cycloaddition products **7a–c** and **8a–c**, respectively. With esters of maleic, fumaric, acrylic and methacrylic acids, mesomeric betaines **6a** and **6b** gave substituted tetralone derivatives. © 2000 Published by Elsevier Science Ltd.

Introduction

Heterocyclic mesomeric betaines[1] have been broadly classified into two types; conjugated heterocyclic mesomeric betaines which are associated with 1,3-dipoles and cross-conjugated heterocyclic mesomeric betaines which are associated with 1,4-dipoles. The dipolar cycloaddition reactions of both types of heterocyclic mesomeric betaines have been widely investigated and this has given access to a diverse variety of heterocyclic molecules. In this paper we report the synthesis of the conjugated heterocyclic mesomeric betaines **6a–c** which posses an azomethine-imine 1,3-dipole. The 1,3-dipolar cycloaddition reactions of mesomeric betaines **6a–c** and the Diels–Alder reactions of their vinylketene valence tautomers **10a–c** are also described.

Synthesis of the Heterocyclic Mesomeric Betaines

The general synthetic route to compounds **6a–c** is shown in Scheme 1. 2-Formylbenzoic acid **1a** was treated with thionyl chloride and then methanol[2] giving a 43:57 mixture of the lactone **2a** and the aldehyde **3a**. This mixture was not separated but was reacted directly with 2-nitrophenylhydrazine



Scheme 1. a, R^1=H; **b**, R^1=Me; **c**, R^1=Ph.

Keywords: mesomeric betaines; cycloadditions; vinylketenes; 1; 3-dipoles.
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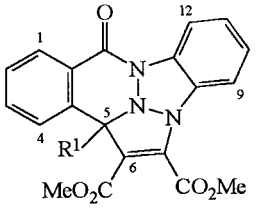
yielding the hydrazone derivative **4a** (84% from **2a**/**3a**). Acid promoted cyclisation of the hydrazone **4a** using toluene-4-sulfonic acid in boiling toluene solution gave the phthalazone derivative **5a** (69%).[3] Reductive cyclisation of compound **5a** with triethyl phosphite at 120°C yielded the heterocyclic mesomeric betaine **6a** (59%) as bronze needles. A 74:26 mixture of the lactone **2b** and ketone **3b** was obtained from the sulfuric acid catalysed esterification reaction of 2-acetylbenzoic acid **1b** with methanol.[4] From this mixture and 2-nitrophenylhydrazine, hydrazone **4b** (70% from **2b/3b**) was obtained. The phthalazone derivative **5b**[5] (63%) was then obtained from acid catalysed cyclisation of **4b** and subsequent triethyl phosphite mediated reductive cyclisation of compound **5b** afforded the heterocyclic mesomeric betaine **6b** (85%) as orange needles. Similarly, methyl 2-benzoylbenzoate **3c** and 2-nitrophenylhydrazine gave the hydrazone **4c** (63%) from which the phthalazone **5c** (71%) was prepared. Reductive cyclisation of compound **5c** with triethyl phosphite gave the heterocyclic mesomeric betaine **6c** (87%) as a dark orange solid.

Reaction of the Heterocyclic Mesomeric Betaines with Acetylenes

All three heterocyclic mesomeric betaines **6a–c** reacted with dimethyl acetylenedicarboxylate in boiling benzene (1.5–5 h) giving the 1,3-dipolar cycloaddition products **7a–c** in good yields (76–93%). The infra-red spectrum ($CHCl_3$) of cycloadduct **7a** showed three carbonyl groups at 1749, 1721, 1658 cm^{-1} which were attributed to the C7 ester, the C6 ester and the lactam groups, respectively. The C6 ester group is observed at significantly lower frequency than the C7 ester group because it is part of an >N–C=C–C=O system. Similarly, the cycloadducts **7b** and **7c** each showed three carbonyl groups (1748, 1722, 1657 cm^{-1} for **7b**; 1745, 1725, 1656 cm^{-1} for **7c**) in their infra-red spectra. The C5 proton of compound **7a** (δ 5.69) and the C5 methyl group (δ 1.99) of compound **7b** were observed as singlets in their ^{1}H NMR spectra.



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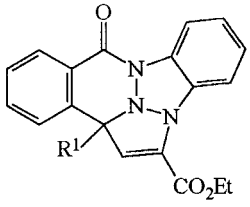

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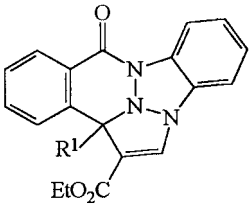

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a, R^1 = H; **b**, R^1 = Me; **c**, R^1 = Ph

When the heterocyclic mesomeric betaines **6a–c** were reacted with ethyl propiolate in boiling benzene (3–168 h) the cycloadducts **8a–c** were obtained in reasonable yields (60–78%). The infra-red spectra of all three cycloadducts indicated the presence of amide (1651–1652 cm^{-1}) and ester (1730–1731 cm^{-1}) groups. When these values are compared with those of the cycloadducts **7a–c** described above, this strongly suggests that these cycloadducts are not associated with an >N–C=C–C=O system. Structures **8a–c** should therefore be assigned to these cycloadducts rather than the corresponding regioisomeric structures **9a–c**. In the ^{1}H NMR spectrum of compound **8a**, the vicinal coupling constant between the C5 and C6 protons was 2.0 Hz although it is conceivable that an allylic coupling constant between the C5 and C7 protons in the regioisomer **9a** might also be of this magnitude. The chemical shifts of the ethoxycarbonyl methylene (δ 4.18–4.24) and methyl (δ 1.23–1.29) protons also support the proposed regioselectivity of the cycloaddition reaction; in regioisomer **9c** the chemical shifts of these protons might be expected to be significantly different than in the compounds **9a** and **9b** because of the proximity of the C5 phenyl substituent.

Semi-empirical molecular orbital calculations also support the observed regioselectivity in the cycloaddition reaction of mesomeric betaine **6a** and ethyl propiolate and these are described later.

The heterocyclic mesomeric betaine **6a** was unreactive towards either diphenylacetylene or *bis*(trimethylsilyl)-acetylene in boiling benzene solution.

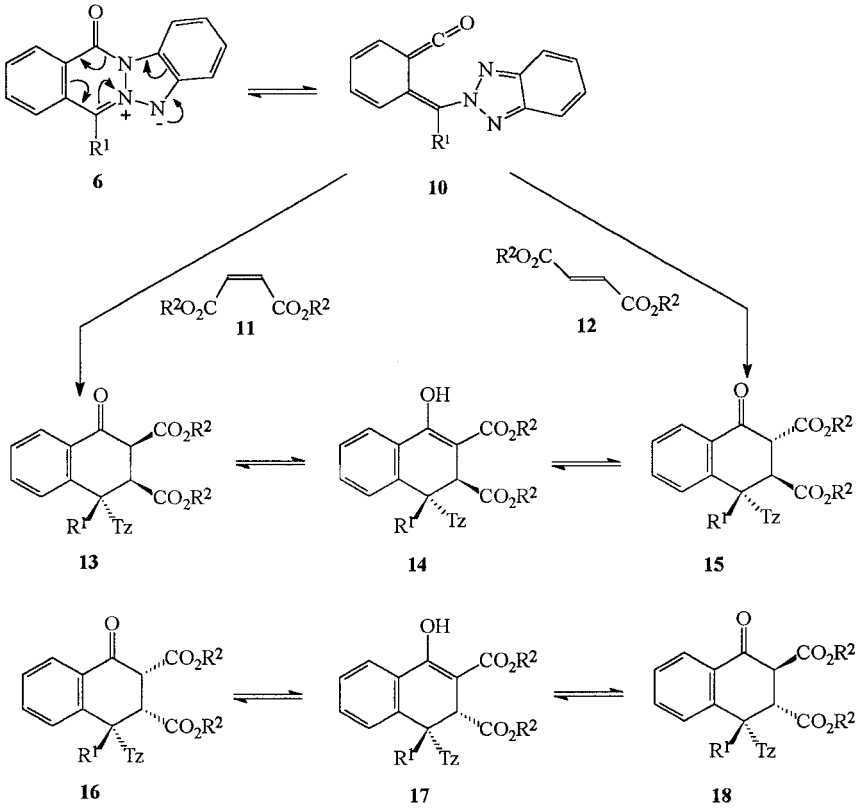
Reaction of the Heterocyclic Mesomeric Betaines with Alkenes

When the heterocyclic mesomeric betaines **6a** and **6b** were reacted with either dimethyl maleate **11** (R^2=Me), diethyl maleate **11** (R^2=Et), dimethyl fumarate **12** (R^2=Me) or diethyl fumarate **12** (R^2=Et) in boiling benzene solution (25–72 h), tetralone derivatives were obtained as outlined in Scheme 2 and Table 1. The formation of these tetralone derivatives can be readily rationalised by invoking a cycloaddition reaction between the vinylketene valence tautomers **10a** and **10b** of the mesomeric betaines **6a** and **6b** with these esters of maleic and fumaric acids. The cycloaddition reactions of the vinylketene intermediates **10a** and **10b** are similar to those of structurally related vinylketenes which have been generated by other routes.[6,7]

In this paper we have considered the formation of the tetralones **13–18** to occur via vinylketene intermediates **10a** and **10b** but we are aware that other reasonable mechanisms for the formation of these products (Scheme 3) could be proposed. In pathway A (Scheme 3) compounds **13–18** are formed via initial Michael addition reactions whereas in pathway B fragmentation of the 1,3-dipolar cycloaddition products could provide an alternative source of the Michael adducts. Pathway B would also rationalise the different product types obtained from the reactions of acetylenic and olefinic dipolarophiles with mesomeric betaines **6a** and **6b**; fragmentation of the acetylene derived cycloadducts **7** and **8** could only result in the formation of vinylic anion intermediates.

Mesomeric betaine **6a** gave a mixture of diastereoisomers **14a** (R^2=Me) and **18a** (R^2=Me) with dimethyl maleate **11** (R^2=Me) which were separated by chromatography (entry 1). The relative stereochemistry of compounds **14a** and **18a** were assigned from their ^{1}H NMR spectra (see below). The formation of these two products can be readily rationalised by assuming that a mixture of the *exo* **13a** and *endo* **16a** cycloadducts are initially formed. Compound **13a** tautomerises giving the enol form **14a** which has the C3 ester and C4 benzotriazole substituents in a favourable *anti* relationship. As a consequence of the *syn* relationships between the C2 and C3 ester substituents in compound **16a**, epimerisation occurs giving the diastereoisomer **18a** via the corresponding enol tautomer **17a**. The co-planar arrangement of the benzene ring, the C1 and C2 carbon atoms in the enol **17a** forces the C3 ester and C4 benzotriazole substituents to lie in almost the same plane, whereas in the ketone **18a** these substituents can lie in different planes. The keto tautomer **18a** is therefore favoured over the corresponding enol tautomer **17a**.

The ^{1}H NMR spectrum of compound **18a** (R^2=Me) exhibited a 12.6 Hz coupling constant between the C2 and C3 protons which is consistent with their proposed *trans*-diaxial relationship. The C4 proton can therefore be *trans*-axial or *cis*-equatorial relative to the C3 proton. The observed coupling constant (4.6 Hz) between the C3 and C4 protons confirms their axial-equatorial relationship. Having established the relative stereochemisry in compound **18a** and hence in the cycloadduct **16a**, the second

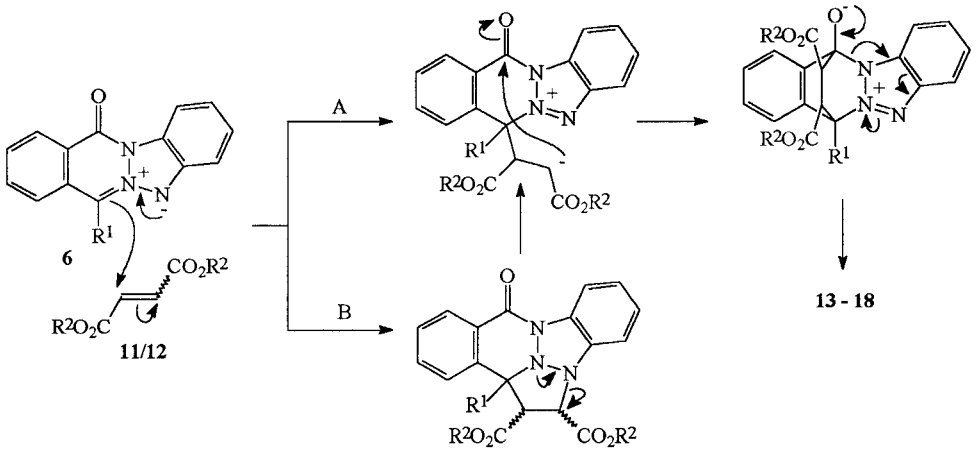


Scheme 2. a, R^1=H; **b**, R^1=Me.

Table 1.

Entry	Mesomeric betaine	Ester	Products[a]
1	**6a**	**11** (R^2=Me)	**14a** (R^2=Me) (31%), **18a** (R^2=Me) (8%)
2	**6a**	**12** (R^2=Me)	**14a** (R^2=Me) (43%), **18a** (R^2=Me) (3%)
3	**6a**	**11** (R^2=Et)	**14a** (R^2=Et) (38%), **18a** (R^2=Et) (17%)
4	**6a**	**12** (R^2=Et)	**14a** (R^2=Et) (73%), **18a** (R^2=Et) (4%)
5	**6b**	**11** (R^2=Me)	**14b/15b** (R^2=Me), 7:3[b] (54%)
6	**6b**	**12** (R^2=Me)	**14b/15b** (R^2=Me), 7:3[b] (56%)
7	**6b**	**11** (R^2=Et)	**14b/15b** (R^2=Et), 13:7[b] (31%)
8	**6b**	**12** (R^2=Et)	**14b/15b** (R^2=Et), 13:7[b] (42%)

[a] Isolated yields.
[b] Ratios determined in by ^{1}H NMR spectroscopy in $CDCl_3$ solution.



Scheme 3.

cycloadduct and its enol tautomer must have the relative stereochemistry depicted in formulae **13a** and **14a**. The coupling constant (2.1 Hz) between the C3 and C4 protons in product **14a** is consistent with their proposed diequatorial orientation.

With dimethyl fumarate **12** (R^2=Me), mesomeric betaine **6a** gave the same mixture of products as with dimethyl maleate **11** (R^2=Me) (entry 2, Table 1). In this reaction, the initially formed cycloadducts are the diastereoisomers **15a** and **18a** with the former compound **15a** tautomerising giving the product **14a**. As noted above, tautomer **18a** is preferred over **17a**. Dimethyl maleate **11** (R^2=Me) was not isomerised to dimethyl fumarate **12** (R^2=Me) under the reaction conditions.

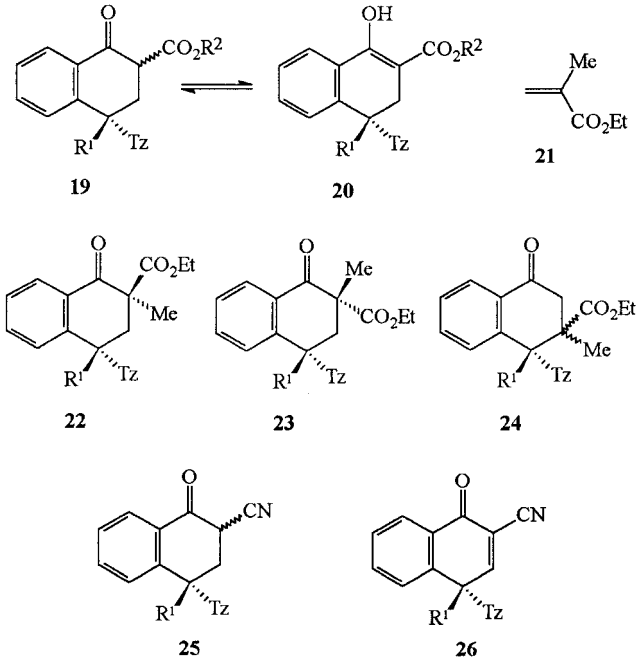
Diethyl maleate **11** (R^2=Et) and diethyl fumarate **12** (R^2=Et) both reacted with mesomeric betaine **6a** giving analogous products **14a** and **18a** to their dimethyl counterparts (entries 3 and 4, respectively, Table 1).

Mesomeric betaine **6b** also reacted with the dimethyl and diethyl esters of maleic and fumaric acids giving an inseparable mixture of diastereoisomers. Crystallisation enabled the isolation of a tautomeric mixture **14b** (R^2=Me, Et)/**15b** (R^2=Me, Et) in the ratios indicated in Table 1. The enol tautomers **14b** are the predominant structures and this contrasts with the exclusive formation of the keto tautomers **15a** described above. The ^{1}H NMR spectrum of tautomers **15b** showed coupling constants (13.7 Hz for R^2=Me; 9.5 Hz for R^2=Et) between the C2 and C3 protons indicating their *trans*-diaxial relationship. These coupling constants would be consistent with either structure **15a** or **18a**. However, we know that in the cycloaddition reactions of **10a**, the enolic product **17a** is disfavoured, and similarly structure **17b** would be expected to be disfavoured. Since an enolic product has been formed, the enol must have the structure **14b**.

Table 2.

Entry	Mesomeric betaine	Acrylate	Product(s)[a]
1	**6a**	Methyl acrylate	**20a** (R^2=Me) (54%)
2	**6b**	Methyl acrylate	**20b** (R^2=Me) (65%)
3	**6a**	Ethyl acrylate	**20a** (R^2=Et) (96%)
4	**6b**	Ethyl acrylate	**20b** (R^2=Et) (97%)
5	**6a**	**21**	**22a** (18%), **23a** (73%)
6	**6b**	**21**	**22b** (15%), **23b** (69%)

[a] Isolated yields



Mesomeric betaines **6a** and **6b** reacted with methyl acrylate, ethyl acrylate and ethyl methacrylate in boiling benzene solution (7–54 h) giving the products indicated in Table 2. All of these reactions were regioselective proceeding with the regiochemistry shown. With methyl and ethyl acrylate, the initially formed cycloadducts **19a/19b** (R^2=Me, Et) tautomerised giving the enols **20a/20b** (R^2=Me, Et). ^{1}H NMR and infra-red spectroscopy fully support the proposed enolic structures and the regiochemistry of these cycloaddition reactions is therefore established; the alternative regiochemistry would not give a β-keto ester and hence enolisation could not occur.

Table 3.

Reactant	HOMO energy (eV)	HOMO coefficients	LUMO energy (eV)	LUMO coefficients
6a	−8.16	C7 (0.522) N5 (−0.489)	−1.26	C7 (−0.276) N5 (−0.321)
Ethyl propiolate	−11.38	C1 (−0.004)[a] C2 (−0.003)	0.20	C1 (0.550)[a] C2 (−0.382)
10a	−8.14	C12 (−0.274)[b] C7 (0.587)	−1.41	C12 (−0.538)[b] C7 (−0.394)
Methyl acrylate	−11.06	C1 (−0.648)[a] C2 (−0.664)	−0.11	C1 (0.652)[a] C2 (−0.497)

[a] C1=β-carbon; C2=α-carbon
[b] The numbering system in **10a** corresponds with **6a** for simplicity.

The cycloaddition reaction of compound **6a** with ethyl methacrylate **21** was regioselective giving a mixture of two stereoisomers **22a** and **23a**. The regioselectivity of the reaction was clear from the ^{1}H NMR spectra of the reaction products. Thus, for compounds **22a** and **23a** an ABX system (δ_A 3.12, δ_B 3.10, δ_X 6.63; J_{AB}=13.2, J_{AX}=10.6, J_{BX}=5.0 Hz) and an AMX system δ_A=2.62, δ_M 3.79, δ_X 6.49; J_{AM}=13.3, J_{AX}=5.2, J_{MX}=12.2 Hz), respectively for the C3 and the C4 protons were observed. In the alternative regio-isomers **24a** these coupling patterns and coupling constants would not be expected. Mesomeric betaine **6b** also reacted with ethyl methacrylate **21** giving a mixture of stereoisomers **22b** and **23b**. Clearly, the structure of the cycloadducts **22b** and **23b** would be anticipated to be analogous to the cycloadducts **22a** and **23a** and this is supported by ^{1}H NMR spectral evidence in which the C3 protons are observed with similar chemical shifts. The assignment of the relative stereochemistry of the cycloadducts **22b** and **23b** is based on the chemical shifts of the methyl protons (δ 1.22 and 0.72, respectively) of the ethoxycarbonyl groups. In the major cycloadduct **23b**, a 1,3-diaxial interaction between the C2 and C4 methyl groups forces the tetralone ring to adopt a conformation in which the methyl protons of the ethoxycarbonyl group lie in the shielding region of the C4 benzotriazole ring and the aromatic ring of the tetralone moiety. Consequently, these protons resonate at lower frequency. The relative stereochemistry of cycloadducts **22a** and **23a** was tentatively assigned as shown because of their general ^{1}H NMR spectral similarity with compounds **22b** and **23b**.

Treatment of mesomeric betaines, **6a** and **6b**, with acrylonitrile in boiling benzene gave a mixture of diastereoisomers (by ^{1}H NMR spectroscopy) but attempted purification of the reaction mixture by chromatography resulted in decomposition. However, the crude reaction product **25b** from the reaction of mesomeric betaine **6b** was successfully oxidised with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in boiling benzene giving compound **26b** although in poor (26%) yield.

Mesomeric betaine **6c** was unreactive towards the alkenes described above and mesomeric betaines **6a** was inert towards ethyl vinyl ether.

Semi-empirical Molecular Orbital Calculations

The PM3 method was used to determine the regioselectivity of the 1,3-dipolar cycloaddition reaction between mesomeric betaine **6a** and ethyl propiolate the Diels–Alder reaction between the vinylketene **10a** and methyl acrylate. The HOMO/LUMO energies of these reactants and their orbital coefficients at the reaction centres are collected in Table 3.

For the mesomeric betaine **6a**/ethyl propiolate reaction the HOMO (**6a**)/LUMO (ethyl propiolate) energy difference is 8.36 eV whereas the HOMO (ethyl propiolate)/LUMO (**6a**) value is 10.57 eV, indicating that this 1,3-dipolar cycloaddition reaction will be controlled by the former interaction. The largest coefficients at the reaction centres of the HOMO of **6a** and the LUMO of ethyl propiolate are located at the C7 and the C1 atoms, respectively, which would predict that the C7 (**6a**)–C1 (ethyl propiolate) bond will be formed. This corresponds with the observed regioselectivity. Additionally, with mesomeric betaines **6b** and **6c**, steric interactions between the R^1 substituent and the ethoxycarbonyl group of the ethyl propiolate would also favour this regioselectivity.

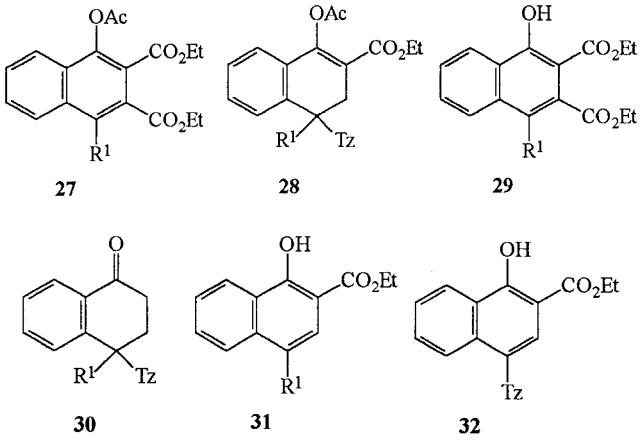
For the vinylketene **10a**/methyl acrylate reaction the HOMO (**10a**)/LUMO (methyl acrylate) energy difference is 8.03 eV whereas the HOMO (methyl acrylate)/LUMO (**10a**) value is 12.47 eV, indicating that this Diels–Alder reaction will be dominated by the former interaction. The largest coefficients at the reaction centres of the HOMO of **10a** and the LUMO of methyl acrylate are located at the C7 and the C1 atoms, respectively, which would predict that the C7 (**10a**)–C1 (methyl acrylate) bond will be formed and this also corresponds with the observed regioselectivity.

Transformations of Cycloadducts

In order to confirm the structures of the cycloaddition products of the valence tautomers **10a** and **10b** of the mesomeric betaines **6a** and **6b**, respectively, some transformations of these cycloadducts were undertaken.

Acetylation of compound **14a** (R^2=Et) with acetic anhydride-pyridine gave 2,3-diethoxycarbonylnaphth-1-yl acetate **27** (84% yield). In this reaction the benzotriazole unit was eliminated and 1-acetylbenzotriazole was detected in the reaction mixture but was partially hydrolysed upon isolation. In contrast, acetylation of the enol esters **20a** (R^2=Et) and **20b** (R^2=Et) with acetic anhydride-pyridine did not result in the elimination of benzotriazole and the

acetates **28a** (57% yield) and **28b** (76% yield), respectively, were isolated. In the case of compound **14a** (R^2=Et) the C3 proton is relatively acidic due to the presence of the C3 ester substituent and hence elimination of benzotriazole is relatively easy.



a, R^1 = H; **b**, R^1 = Me

Compound **14a** (R^2=Et) reacted with a catalytic quantity of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in boiling benzene giving the naphthalene derivative **29a**[8] (68%) and benzotriazole (64%). Similarly, treatment of a tautomeric mixture of compounds **14b/15b** (R^2=Et) with DBN afforded the naphthalene derivative **29b** (77%) and benzotriazole (69%). In contrast, the enol ester **20a** did not react under these conditions indicating the necessity of a relatively acidic C3 proton for the elimination of benzotriazole.

Alkaline hydrolysis of the enol esters **20a** (R^2=Et) and **20b** (R^2=Et) gave the substituted tetralone derivative **30a** (88% yield) and **30b** (56%), respectively. Acidic hydrolysis of compound **20a** (R^2=Et) resulted only in partial hydrolysis of the ester group and a mixture of the tetralone **30a** (41%), the ester **31a**[9] (31%) and benzotriazole (41% yield) was obtained. Ester derivative **20b** (R^2=Et) gave a mixture of compound **31b** (58%) and benzotriazole (65%) under similar conditions.

Oxidation of compound **20a** (R^2=Et) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave the naphthalene derivative **32** (85%).

Conclusions

The heterocyclic mesomeric betaines **6a–c** underwent typical 1,3-dipolar cycloaddition reactions with DMAD and ethyl propiolate. With electron deficient alkenes they gave tetralone derivatives possibly via Diels–Alder reactions of their valence tautomers **10a–c**. The regioselectivity of both types of cycloaddition reaction has been established and rationalised by semi-empirical molecular orbital calculations.

Experimental

^{1}H NMR spectra were determined at 220 or 400 MHz in $CDCl_3$ solution. Infra-red spectra were recorded in $CHCl_3$ solution unless stated otherwise. Chromatography refers to preparative thick layer chromatography using silica gel coated glass plates.

3-Methoxyphthalide 2a and 2-methoxycarbonylbenzaldehyde 3a.[2] Compound **1a** (20 g, 0.13 mol) and thionyl chloride (20 mL, 0.28 mol) were heated (2 h) at reflux. The reaction mixture was allowed to cool to room temperature and evaporated. Methanol (60 mL) was added to the residue and the mixture was heated (4 h) at reflux, allowed to cool to room temperature, evaporated and then distilled under reduced pressure giving a 43:57 mixture (18.2 g) of compounds **2a** and **3a** as a colourless oil, bp 150–152°C, 1 mm Hg. Compound **2a**: δ_H (220 MHz) 7.62 (4H, m, Ar*H*), 6.31 (1H, s, C3–*H*) and 3.62 (3H, s, –OCH_3). Compound **3a**: δ_H (220 MHz) 10.57 (1H, s, –C*H*O), 7.91 (4H, m, Ar*H*) and 3.97 (3H, s, –CO_2CH_3).

3-Methyl-3-methoxyphthalide 2b and methyl 2-acetylbenzoate 3b.[4] A mixture of compound **1b** (20 g, 0.12 mol), methanol (40 mL) and concentrated sulphuric acid (2 mL) was stored (15 h) at room temperature. The mixture was poured into water (70 mL) and extracted with ether (3×40 mL). The combined organic extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was distilled under reduced pressure giving a 74:26 mixture (16.2 g) of compounds **2b** and **3b** as a colourless oil, bp 120–122°C, 8 mm Hg. Compound **2b**: δ_H (220 MHz) **2b** 7.57 (4H, m, Ar*H*), 3.05 (3H, s, –OCH_3) and 1.84 (3H, s, –CH_3). Compound **3b**: δ_H (220 MHz) 7.82 (4H, m, Ar*H*), 3.90 (3H, s, –OCO_2CH_3) and 2.54 (3H, s, –COCH_3).

2-Methoxycarbonylbenzaldehyde 2′-nitrophenylhydrazone 4a. 2-Nitrophenylhydrazone (4.0 g, 26 mmol) was dissolved in hot ethanol (150 mL). The solution was cooled in an ice-bath and concentrated hydrochloric acid (1 mL) followed by a mixture of **2a/3a** (10.0 g) prepared as described above was added. The reaction was kept (1 h) in the cold and the orange precipitate of compound **4a** (6.57 g, 84% from **3a**) was collected, mp 186–187°C (with sublimation before melting) (from methanol–chloroform). (Found: C, 60.7; H, 4.6; N, 13.8. $C_{15}H_{13}N_3O_4$ requires C, 60.2; H, 4.4; N, 14.0%), $\nu_{max.}$ 3310, 1717, 1619, 1578, 1503, 1483, 1334, 1275, 1258 and 1144 cm^{-1}, δ_H (220 MHz) 11.09 (1H, s, >N*H*), 8.87 (1H, s, –C*H*=), 8.17 (2H, m, Ar*H*), 7.96 (2H, m, Ar*H*), 7.54 (2H, m, Ar*H*), 7.41 (1H, dt, *J*=7.7 and 1.3 Hz, Ar*H*), 6.83 (1H, dt, *J*=7.9 and 1.2 Hz, Ar*H*) and 3.94 (3H, s, –CO_2CH_3).

2-Methoxycarbonylacetophenone 2′-nitrophenylhydrazone 4b. A mixture of compounds **2b/3b** (10.0 g), prepared as described above, was added to a solution of 2-nitrophenylhydrazone (2.24 g, 15 mmol) and concentrated hydrochloric acid (1 mL) in methanol (40 mL). The mixture was heated (1 h) at reflux, allowed to cool to room temperature and methanol (160 mL) and water (40 mL) were added. The solution was decanted from the resulting oil and water was added. The cloudy mixture was allowed to stand (15 h) and the orange precipitate collected yielding compound **4b** (3.2 g, 70% from **3b**), mp 101–102°C (from 70% aqueous ethanol). (Found: C, 61.6; H, 4.9; N, 13.6. $C_{16}H_{15}N_3O_4$ requires C, 61.3; H, 4.8; N, 13.4%), $\nu_{max.}$ 3335, 1723,

1609, 1581, 1503, 1294, 1271 and 1145 cm^{-1}, δ_H (220 MHz) 10.89 (1H, s, >N*H*), 8.15 (1H, dd, *J*=8.8 and 1.7 Hz, Ar*H*), 7.82 (2H, m, Ar*H*), 7.48 (4H, m, Ar*H*), 6.81 (1H, dt, *J*=7.6 and 1.3 Hz, Ar*H*) 3.81 (3H, s, $-CO_2CH_3$) and 2.36 (3H, m, $-CH_3$).

2-Methoxycarbonylbenzophenone 2′-nitrophenylhydrazone 4c. Compound **3c**[10] (7.0 g, 29 mmol), 2-nitrophenylhydrazone (4.46 g, 29 mmol), concentrated hydrochloric acid (2 mL) and methanol (70 mL) were heated (22 h) at reflux with stirring. The reaction mixture was allowed to cool to room temperature and kept (15 h) giving compound **4c** (6.86 g, 63%) as red crystals, mp 160–161°C (from ethanol). (Found: C, 66.9; H, 4.5; N, 11.3. $C_{21}H_{17}N_3O_4$ requires C, 67.2; H, 4.6; N, 11.2%), $\nu_{max.}$ 3300, 1726, 1615, 1575, 1492, 1320, 1273 and 1140 cm^{-1}, δ_H (220 MHz) 10.55 (1H, s, >N*H*), 8.29 (1H, dd, *J*=7.8 and 1.1 Hz, Ar*H*), 8.13 (1H, d, *J*=8.3 Hz, Ar*H*), 8.08 (1H, dd, *J*=8.8 and 1.1 Hz, Ar*H*), 7.79 (1H, dt, *J*=8.8 and 1.3 Hz, Ar*H*), 7.62 (3H, m, Ar*H*), 7.34 (5H, m, –*Ph*), 6.79 (1H, dt, *J*=7.0 and 1.1 Hz, Ar*H*) and 3.68 (3H, s, $-CO_2CH_3$).

3-(2′-Nitrophenyl)phthalaz-4-one 5a. A mixture of compound **4a** (5.8 g, 19 mmol), toluene-4-sulfonic acid (1.0 g) and toluene (15 mL) was heated (47 h) at reflux. The mixture was allowed to cool to room temperature, evaporated and ethanol (40 mL) was added to the residue. The solid was collected, washed with ethanol and recrystallised from ethanol giving compound **5a** (3.5 g, 69%) as white needles, mp 204–206°C (lit.[3] mp 201°C). $\nu_{max.}$ 1673, 1536, 1360 and 1338 cm^{-1}, δ_H (440 MHz) 8.66 (1H, d, *J*=0.9 Hz, C1–*H*), 8.30 (1H, ddd, *J*=8.0, 1.1 and 0.9 Hz, Ar*H*), 8.16 (1H, dd, *J*=8.1 and 1.5 Hz, Ar*H*), 8.06 (2H, m, Ar*H*), 7.95 (2H, m, Ar*H*), 7.83 (1H, dd, *J*=8.1 and 1.5 Hz, Ar*H*) and 7.75 (1H, dt, *J*=8.1, 7.4 and 1.5 Hz, Ar*H*).

1-Methyl-3-(2′-nitrophenyl)phthalaz-4-one 5b. Using a similar method to that described above for the preparation of compound **5a**, compound **4b** (4.7 g, 15 mmol), toluene-4-sulfonic acid (1.0 g) and toluene (10 mL) at reflux (9 h) gave compound **5b** (2.65 g, 63%) as white crystals, mp 203–204°C (from ethanol) (lit.[5] mp 202°C). $\nu_{max.}$ 1669, 1609, 1597, 1534, 1353 and 1340 cm^{-1}, δ_H (400 MHz) 8.49 (1H, d, *J*=8.1 Hz, Ar*H*), 8.08 (1H, dd, *J*=8.0 and 1.5 Hz, Ar*H*), 7.89 (1H, dt, *J*=8.1, 7.0 and 1.2 Hz, Ar*H*), 7.82 (2H, m, Ar*H*), 7.76 (1H, dt, *J*=7.8 and 1.5 Hz, Ar*H*), 7.69 (1H, dd, *J*=7.8 and 1.5 Hz, Ar*H*), 7.57 (1H, dt, *J*=7.8 and 1.8 Hz, Ar*H*) and 2.65 (3H, s, $-CH_3$).

1-Phenyl-3-(2′-nitrophenyl)phthalaz-4-one 5c. Using a similar method to that described above for the preparation of compound **5a**, compound **4c** (5.0 g, 15 mmol), toluene-4-sulfonic acid (1.0 g) and toluene (15 mL) at reflux (43 h) gave compound **5c** (3.26 g, 71%) as white crystals, mp 163–164°C (from ethanol). (Found: C, 69.9; H, 3.8; N, 12.2. $C_{20}H_{13}N_3O_3$ requires C, 70.0; H, 3.8; N, 12.2%), $\nu_{max.}$ 1670, 1609, 1589, 1533, 1359 and 1340 cm^{-1}, δ_H (400 MHz) 8.57 (1H, m, Ar*H*), 8.09 (1H, ddd, *J*=8.1, 1.3 and 0.5 Hz, Ar*H*), 7.82 (3H, m, Ar*H*), 7.76 (3H, m, Ar*H*) and 7.56 (5H, m, –*Ph*).

5,12-Dihydro-12-oxo-6λ^5-phthalazino[2,3-a]benzotriazole-6-ylium-5-ide 6a. A mixture of compound **5a** (2.0 g, 7.5 mmol) and freshly distilled triethyl phosphite (15 mL) was heated (65 h) at 120°C under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and the solid collected by filtration giving compound **6a** (1.04 g, 59%) as bronze needles, mp 249–250°C (with sublimation before melting) (from CH_3CN). (Found: C, 71.2; H, 4.0; N, 17.6 $C_{14}H_9N_3O$ requires C, 71.5; H, 3.9; N, 17.9%), $\nu_{max.}$ 1665, 1609, 1539 and 1148 cm^{-1}, $\lambda_{max.}$ (EtOH) 238, 253, 277, 319, 401, 444 and 460 nm, δ_H (440 MHz) 8.66 (1H, ddd, *J*=8.2, 1.2 and 0.8 Hz, Ar*H*), 8.50 (1H, ddd, *J*=8.2, 1.3 and 0.6 Hz, Ar*H*), 8.39 (1H, s, Ar*H*), 7.72 (1H, dt, *J*=8.1, 6.8 and 1.3 Hz, Ar*H*), 7.62 (2H, m, Ar*H*), 7.56 (1H, dt, *J*=8.4, 7.3 and 1.2 Hz, Ar*H*), 7.50 (1H, dt, *J*=8.2, 6.8 and 1.3 Hz, Ar*H*) and 7.33 (1H, dt, *J*=8.2, 7.3 and 1.3 Hz, Ar*H*).

7-Methyl-5,12-dihydro-12-oxo-6λ^5-phthalazino[2,3-a]-benzotriazole-6-ylium-5-ide 6b. Using a similar method to that described above for the preparation of compound **6a**, compound **5b** (2.0 g, 7 mmol) and triethyl phosphite (15 mL) gave, after 48 h, compound **6b** (1.51 g, 85%) as orange needles, mp 268–270°C (with sublimation before melting) (from CH_3CN). (Found: C, 72.0; H, 4.6; N, 16.7. $C_{15}H_{11}N_3O$ requires C, 72.3; H, 4.5; N, 16.9%), $\nu_{max.}$ (KBr) 1654, 1603, 1520, 1429, 1311, 1254, 1191 and 748 cm^{-1}, $\lambda_{max.}$ (EtOH) 209, 225, 249, 252, 276, 407, 453 and 470 nm, δ_H (400 MHz) 8.67 (1H, ddd, *J*=8.2, 1.2 and 0.7 Hz, Ar*H*), 8.60 (1H, ddd, *J*=8.2, 1.4 and 0.7 Hz, Ar*H*), 7.84 (1H, ddd, *J*=8.5, 1.4 and 0.7 Hz, Ar*H*), 7.80 (1H, dt, *J*=8.5, 6.5 and 1.4 Hz, Ar*H*), 7.66 (1H, ddd, *J*=8.4, 1.0 and 0.6 Hz, Ar*H*), 7.55 (1H, dt, *J*=8.4, 7.3 and 1.2 Hz, Ar*H*), 7.52 (1H, dt, *J*=8.5, 8.2 and 1.4 Hz, Ar*H*), 7.30 (1H, dt, *J*=8.2, 7.3 and 1.0 Hz, Ar*H*) and 3.01 (3H, s, $-CH_3$).

7-Phenyl-5,12-dihydro-12-oxo-6λ^5-phthalazino[2,3-a]-benzotriazole-6-ylium-5-ide 6c. Using a similar method to that described above for the preparation of compound **6a**, compound **5c** (2.0 g, 5.8 mmol) and triethyl phosphite (15 mL) gave, after 24 h, compound **6c** (1.57 g, 87%) as a dark orange solid, mp 291–292°C (with sublimation before melting) (from CH_3CN). (Found: C, 76.9; H, 4.4; N, 13.4. $C_{20}H_{13}N_3O$ requires C, 77.2; H, 4.2; N, 13.5%), $\nu_{max.}$ (KBr) 1673, 1607, 1515, 1479, 1434, 1129 and 750 cm^{-1}, $\lambda_{max.}$ (EtOH) 208, 226, 253, 280, 288, 322, 416 and 472 nm, δ_H (400 MHz) 8.73 (1H, d, *J*=8.3 Hz, Ar*H*), 8.61 (1H, ddd, *J*=8.1, 1.3 and 0.8 Hz, Ar*H*), 7.66 (5H, m, Ar*H*), 7.60 (2H, m, Ar*H*), 7.50 (3H, m, Ar*H*) and 7.33 (1H, dt, *J*=8.3, 7.1 and 1.1 Hz, Ar*H*).

6,7-Dimethoxycarbonyl-5a,8,13-nitrilodibenzo[b,f][1,4]-diazecin-14(5H)-one 7a. A mixture of compound **6a** (0.75 g, 3.2 mmol), DMAD (0.8 mL, 6.5 mmol) and benzene (30 mL) was heated at reflux (1.5 h). The reaction mixture was allowed to cool to room temperature, evaporated and the residue was triturated with ethanol (15 mL) giving compound **7a** (0.91 g, 76%) as pale yellow crystals, mp 211–212°C (with softening at 178°C) (from ethanol). (Found: C, 63.8; H, 4.2; N, 10.9, M 377.1006. $C_{20}H_{15}N_3O_5$ requires C, 63.7; H, 4.0; N, 11.1%, M 377.1011). $\nu_{max.}$ 1749, 1721, 1658, 1482, 1441, 1410, 1348 and 1300 cm^{-1}, δ_H (400 MHz) 8.24 (1H, ddd, *J*=7.7, 1.4 and 0.6 Hz, Ar*H*), 8.06 (1H, ddd, *J*=7.6, 1.2 and 0.6 Hz, Ar*H*), 7.66 (2H, m, Ar*H*), 7.57 (1H, dt,

J=7.7, 6.8 and 1.8 Hz, Ar*H*), 7.34 (1H, dt, J=7.6 and 1.2 Hz, Ar*H*), 7.28 (1H, ddd, J=7.6, 1.2 and 0.6 Hz, Ar*H*), 7.13 (1H, dt, J=7.6 and 1.2 Hz, Ar*H*), 5.69 (1H, s, C5-*H*), 3.76 (3H, s, $-OCH_3$) and 3.63 (3H, s, $-OCH_3$).

6,7-Dimethoxycarbonyl-5-methyl-5a,8,13-nitrilodibenzo-[b,f][1,4]diazecin-14(5H)-one 7b. Using a similar method to that described above for the preparation of compound **7a**, compound **6b** (0.75 g, 3.0 mmol) and DMAD (0.8 mL, 6.5 mmol) in benzene (15 mL) gave, after 1.5 h, compound **7b** (1.05 g, 89%) as yellow crystals, mp 181–183°C (from EtOH). (Found: C, 64.6; H, 4.4; N, 10.8, M 391.1146. $C_{21}H_{17}N_3O_5$ requires C, 64.5; H, 4.4; N, 10.7%, M 391.1168). $\nu_{max.}$ 1748, 1722, 1657, 1485, 1415 and 1301 cm^{-1}, δ_H (400 MHz) 8.26 (1H, dd, J=8.0 and 1.6 Hz, Ar*H*), 8.05 (1H, dd, J=7.8 and 1.3 Hz, Ar*H*), 7.78 (1H, dd, J=8.0 and 1.2 Hz, Ar*H*), 7.67 (1H, dt, J=8.0 and 1.6 Hz, Ar*H*) 7.54 (1H, dt, J=8.0 and 1.2 Hz, Ar*H*), 7.33 (1H, dt, J=7.8 and 1.2 Hz, Ar*H*), 7.28 (1H, d, J=7.8 Hz, Ar*H*), 7.13 (1H, dt, J=7.8 and 1.3 Hz, Ar*H*), 3.75 (3H, s, $-OCH_3$), 3.63 (3H, s, $-OCH_3$) and 1.99 (3H, s, $-CH_3$).

6,7-Dimethoxycarbonyl-5-phenyl-5a,8,13-nitrilodibenzo-[b,f][1,4]diazecin-14(5H)-one 7c. Using a similar method to that described above for the preparation of compound **7a**, compound **6c** (1.0 g, 3.2 mmol) and DMAD (0.8 mL, 6.5 mmol) in benzene (30 mL) gave, after 5 h, compound **7c** (93%) as yellow crystals, mp 261–264°C (from ethanol). (Found: C, 68.9; H, 4.5; N, 9.0, M 453.1326. $C_{26}H_{19}N_3O_5$ requires C, 68.9; H, 4.2; N, 9.3%, M 453.1327). $\nu_{max.}$ 1745, 1725, 1656, 1483 and 1413 cm^{-1}, δ_H (400 MHz) 8.29 (1H, dd, J=7.8 and 2.0 Hz, Ar*H*), 8.09 (1H, dd, J=7.8 and 1.1 Hz, Ar*H*), 7.50 (3H, m, Ar*H*), 7.46 (1H, dt, J=7.8 and 2.0 Hz, Ar*H*), 7.40 (3H, m, Ar*H*), 7.33 (1H, dt, J=7.8 and 1.1 Hz, Ar*H*), 7.18 (1H, d, J=7.8 Hz, Ar*H*), 7.09 (1H, dt, J=7.8 and 1.1 Hz, Ar*H*), 7.03 (1H, dd, J=7.8 and 2.0 Hz, Ar*H*), 3.76 (3H, s, $-OCH_3$) and 3.66 (3H, s, $-OCH_3$).

7-Ethoxycarbonyl-5a,8,13-nitrilodibenzo[b,f][1,4]diazecin-14(5H)-one 8a. A mixture of compound **6a** (200 mg, 0.85 mmol), ethyl propiolate (0.1 mL, 0.98 mmol) and benzene (10 mL) was heated at reflux (3 h) with stirring. The reaction mixture was allowed to cool to room temperature, evaporated and the residual yellow oil was triturated with ether (7 mL) giving compound **8a** (195 mg, 69%) as yellow needles, mp 146–148°C (from ethanol). (Found: C, 68.3; H, 4.6; N, 12.8, M 333.1110. $C_{19}H_{15}N_3O_3$ requires: C, 68.5; H, 4.5; N, 12.6%, M 333.1113), $\nu_{max.}$ 1731, 1652, 1484, 1411, 1315 and 1102 cm^{-1}, δ_H (220 MHz) 8.28 (1H, dd, J=7.1 and 1.2 Hz, Ar*H*), 8.06 (1H, d, J=7.6 Hz, Ar*H*), 7.69 (1H, d, J=7.6 Hz, Ar*H*), 7.58 (2H, m Ar*H*), 7.44 (1H, d, J=7.6 Hz, Ar*H*), 7.29 (1H, dt, J=7.6 and 1.2 Hz, Ar*H*), 7.13 (1H, dt, J=7.6 and 1.2 Hz, Ar*H*), 6.22 (1H, d, J=2.0 Hz, C6–*H*), 5.59 (1H, d, J=2.0 Hz, C5–*H*), 4.20 (2H, m, $-OCH_2CH_3$) and 1.25 (3H, t, J=7.3 Hz, $-OCH_2CH_3$).

7-Ethoxycarbonyl-5-methyl-5a,8,13-nitrilodibenzo[b,f][1,4]-diazecin-14(5H)-one 8b. A mixture of compound **6c** (200 mg, 0.80 mmol) and ethyl propiolate (0.1 mL, 0.98 mmol) and benzene (10 mL) was heated at reflux (24 h) with stirring. The reaction mixture was allowed to cool to room temperature, evaporated and the residual oil was dissolved in boiling benzene–hexane (1:8) (70 mL). The solution was stored at room temperature (15 h) giving a complex of compound **8b**·0.5 benzene (185 mg, 60%), mp 115–118°C (with softening at 100°C). (Found: C, 71.7; H, 5.2; N, 10.8, M 347.1273. $C_{20}H_{17}N_3O_3{\cdot}0.5C_6H_6$ requires C, 71.5; H, 5.2; N, 10.9%, M 347.1270). $\nu_{max.}$ 1730, 1652, 1485, 1415, 1313, 1130 and 1072 cm^{-1}, δ_H (220 MHz) 8.28 (1H, dd, J=7.6 and 1.7 Hz, Ar*H*), 8.02 (1H, dd, J=7.7 and 1.1 Hz, Ar*H*), 7.62 (2H, m, Ar*H*), 7.49 (2H, m, Ar*H*), 7.32 (3H, s, benzene), 7.25 (1H, dt, J=7.7 and 1.4 Hz, Ar*H*), 7.10 (1H, dt, J=7.7 and 1.1 Hz, Ar*H*), 6.22 (1H, s, C6–*H*), 4.18 (2H, m, $-OCH_2CH_3$), 1.85 (3H, s, $-CH_3$) and 1.23 (3H, t, J=7.6 Hz, $-OCH_2CH_3$).

7-Ethoxycarbonyl-5-phenyl-5a,8,13-nitrilodibenzo[b,f][1,4]-diazecin-14(5H)-one 8c. A mixture of compound **6c** (200 mg, 0.64 mmol), ethyl propiolate (0.1 mL, 0.98 mmol) and benzene (10 mL) was heated at reflux (168 h) with stirring. The reaction mixture was allowed to cool to room temperature, evaporated and the residual yellow oil was triturated with ether (5 mL) giving compound **8c** (205 mg, 78%) as yellow crystals, mp 208–210°C (from ethanol). (Found: C, 73.3; H, 4.7; N, 10.1, M 409.1420. $C_{25}H_{19}N_3O_3$ requires C, 73.3; H, 4.7; N, 10.3%, M 409.1414). $\nu_{max.}$ 1731, 1651, 1485, 1413, 1310 and 1108 cm^{-1}, δ_H (220 MHz) 8.33 (1H, dd, J=7.3 and 1.7 Hz, Ar*H*), 8.11 (1H, d, J=7.7 Hz, Ar*H*), 7.65–7.35 (8H, m, Ar*H*), 7.29 (1H, dt, J=7.7 and 1.1 Hz, Ar*H*), 7.11 (1H, dt, J=7.7 and 1.1 Hz, Ar*H*), 6.92 (1H, m, Ar*H*), 6.68 (1H, s, C6–*H*), 4.24 (2H, m, $-OCH_2CH_3$) and 1.29 (3H, t, J=7.6 Hz, $-OCH_2CH_3$).

(3α,4β)-4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2,3-dimethoxycarbonylnaphth-1-ol 14a (R^2=Me) and (2α,3β,4β)-4-(2′H-benzotriazol-2′-yl)-2,3-dimethoxycarbonyltetra-1-one 18a (R^2=Me). *(Method A)* From dimethyl maleate **11** (R^2=Me): a mixture of compound **6a** (204 mg, 0.87 mmol) dimethyl maleate **11** (R^2=Me) (0.13 mL, 1.04 mmol) and benzene (10 mL) was heated at reflux (32 h) with stirring. The reaction mixture was allowed to cool to room temperature, evaporated and the residue was fractionated by chromatography (light petroleum bp 40–60°C: ethyl acetate, 3:1) giving compound **14a** (R^2=Me) (R_f 0.47) (103 mg, 31%) as white needles, mp 148.5–149.5°C (from 70% aqueous ethanol) and compound **18a** (R^2=Me) (R_f 0.27) (27 mg, 8%) as small white needles, mp 188–190°C (from ethanol). Compound **14a** (R^2=Me): (Found: C, 63.1; H, 4.8; N, 11.3, M 379.1178. $C_{20}H_{17}N_3O_5$ requires C, 63.3; H, 4.5; N, 11.1%, M 379.1168). $\nu_{max.}$ 1744, 1659, 1625, 1578, 1445, 1359 and 1278 cm^{-1}, δ_H (220 MHz) 12.61 (1H, s, –OH), 8.03 (1H, d, J=8.0 Hz, Ar*H*), 7.79 (2H, m, Ar*H*), 7.48 (3H, m, Ar*H*), 7.31 (2H, m, Ar*H*), 6.57 (1H, d, J=2.1 Hz, C4–*H*), 4.77 (1H, d, J=2.1 Hz, C3–*H*), 3.78 (3H, s, $-OCH_3$) and 3.68 (3H, s, $-OCH_3$). Compound **18a** (R^2=Me): (Found: C, 63.5; H, 4.6; N, 11.3, M 379.1166. $C_{20}H_{17}N_3O_5$ requires C, 63.3; H, 4.5; N, 11.1%, M 379.1168). $\nu_{max.}$ 1744, 1693, 1438, 1325, 1263 and 1160 cm^{-1}, δ_H (220 MHz) 8.18 (1H, d, J=7.6 Hz, Ar*H*), 7.78 (2H, m, Ar*H*), 7.56 (3H, m, Ar*H*), 7.35 (2H, m, Ar*H*), 6.77 (1H, d, J=4.6 Hz, C4–*H*), 4.95 (1H, d, J=12.6 Hz, C2–*H*), 4.31 (1H, dd, J=12.6 and 4.6 Hz, C3–*H*), 3.88 (3H, s, $-OCH_3$) and 3.63 (3H, s, $-OCH_3$).

Method B. From dimethyl fumarate **12** (R^2=Me): when

dimethyl maleate **11** (R^2=Me) was replaced with dimethyl fumarate **12** (R^2=Me) in Method A above, compounds **14a** (R^2=Me) (43%) and **18a** (R^2=Me) (3%), both identical with authentic samples, were obtained after chromatography.

(3α,4β)-4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2,3-diethoxycarbonylnaphth-1-ol 14a (R^2=Et) and (2α,3β,4β)-4-(2′H-benzotriazol-2′-yl)-2,3-diethoxycarbonyltetra-1-one 18a (R^2=Et). *(Method A)* From diethyl maleate: using a similar method to that described above for the preparation of compounds **14a** (R^2=Me) and **18a** (R^2=Me) but with a reflux period of 72 h, compound **6a** (200 mg, 0.85 mmol) diethyl maleate **11** (R^2=Et) (0.3 mL, 1.84 mmol) and benzene (15 mL) gave compound **14a** (R^2=Et) (R_f 0.59) (131 mg, 38%) as white needles, mp 95–97°C (from 70% aqueous ethanol) and compound **18a** (R^2=Et) (R_f 0.44) (60 mg, 17%) as white needles, mp 117–118°C (from 50% aqueous ethanol) after chromatography. Compound **14a** (R^2=Et): (Found: C, 65.0; H, 5.4; N, 10.2, M 407.1469. $C_{22}H_{21}N_3O_5$ requires C, 64.9; H, 5.2; N, 10.3%, M 407.1481). $\nu_{max.}$ 1746, 1655, 1589, 1548, 1406, 1375, 1359, 1277, 1092 and 1020 cm^{-1}, δ_H (220 MHz) 12.69 (1H, s, –OH), 8.02 (1H, dd, *J*=7.9 and 1.4 Hz, Ar*H*), 7.78 (2H, m, Ar*H*), 7.46 (3H, m, Ar*H*), 7.30 (2H, m, Ar*H*), 6.54 (1H, d, *J*=2.4 Hz, C4–*H*), 4.73 (1H, d, *J*=2.4 Hz, C3–*H*), 4.20 (4H, m, 2×–OCH_2CH$_3$), 1.24 (3H, t, *J*=7.2 Hz, –OCH_2CH$_3$) and 1.15 (3H, t, *J*=7.2 Hz, –OCH_2CH$_3$). Compound **18a** (R^2=Et): (Found: C, 65.0; H, 5.3; N, 10.4, M 407.1492. $C_{22}H_{21}N_3O_5$ requires C, 64.9; H, 5.2; N, 10.3%, M 407.1481). $\nu_{max.}$ 1739, 1693, 1604, 1586, 1373, 1325, 1261 and 1106 cm^{-1}, δ_H (400 MHz) 8.17 (1H, dd, *J*=8.5 and 2 Hz, Ar*H*), 7.78 (2H, m, Ar*H*), 7.57 (3H, m, Ar*H*), 7.34 (2H, m, Ar*H*), 6.77 (1H, d, *J*=4.9 Hz, C4–*H*), 4.95 (1H, d, *J*=12.8 Hz, C2–*H*), 4.32 (3H, m, C3–*H* and –OCH_2CH$_3$), 4.05 (2H, m, –OCH_2CH$_3$), 1.36 (3H, t, *J*=7.4 Hz, –OCH_2CH$_3$) and 1.07 (3H, t, *J*=7.4 Hz, –OCH$_2$CH_3).

Method B. From diethyl fumarate **12** (R^2=Et): when diethyl maleate **11** (R^2=Et) was replaced with diethyl fumarate **12** (R^2=Et) in Method A above, compounds **14a** (R^2=Et) (73%) and **18a** (R^2=Et) (4%) were obtained after chromatography, identical with authentic samples.

(3α,4β)-4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2,3-dimethoxycarbonyl-4-methylnaphth-1-ol 14b (R^2=Me) and (2α,3β,4α)-4-(2′H-benzotriazol-2′-yl)-2,3-dimethoxycarbonyl-4-methyltetra-1-one 15b (R^2=Me). *(Method A)* From dimethyl maleate **11** (R^2=Me): using a method similar to that described above for the preparation of compounds **14a** (R^2=Me) and **18a** (R^2=Me) but with a reflux period of 196 h, compound **6b** (201 mg, 0.81 mmol), dimethyl maleate **11** (R^2=Me) (0.13 mL, 1.04 mmol) and benzene (10 mL) gave compounds **14b/15b** (R^2=Me) (170 mg, 54%) as white crystals, mp 156–159°C (from 50% aqueous ethanol). (Found: C, 63.9; H, 5.0; N, 10.9, M 393.1349. $C_{21}H_{19}N_3O_5$ requires C, 64.1; H, 4.9; N, 10.7%, M 393.1325). $\nu_{max.}$ 1738, 1693, 1657, 1624, 1575, 1444, 1360, 1323, 1270 and 999 cm^{-1}, δ_H (220 MHz) 12.34 (s, enol –OH) 8.15–7.20 (m, Ar*H*), 6.49 (m, Ar*H*), 5.22 (s, enol C3–*H*), 5.01 (d, *J*=13.7 Hz, keto C2–*H*), 4.29 (d, *J*=13.7 Hz, keto C3–*H*), 3.83 (s, keto –OCH_3), 3.78 (s, enol –OCH_3), 3.60 (s, enol –OCH_3), 3.27 (s, keto –OCH_3), 2.28 (s, keto C4–CH_3) and 2.20 (s, enol C4–CH_3). The enol: keto ratio in $CDCl_3$ solution was determined as 7:3.

Method B. From dimethyl fumarate **12** (R^2=Me): when dimethyl maleate **11** (R^2=Me) was replaced with dimethyl fumarate **12** (R^2=Me) in Method A above, compounds **14b/15b** (R^2=Me) (56%) were obtained after chromatography, identical with an authentic sample.

(3α,4β)-4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2,3-diethoxycarbonyl-4-methylnaphth-1-ol 14b (R^2=Et) and (2α,3β,4α)-4-(2′H-benzotriazol-2′-yl)-2,3-diethoxycarbonyl-4-methyltetra-1-one 15b (R^2=Et). *(Method A)* From diethyl maleate **11** (R^2=Et): using a similar method to that described above for the preparation of compounds **14b/15b** (R^2=Me) but with a reflux period of 168 h, compound **6b** (200 mg, 0.80 mmol), diethyl maleate **11** (R^2=Et) (0.3 mL, 1.86 mmol) and benzene (10 mL) gave compounds **14b/15b** (R^2=Et) (105 mg, 31%) as white crystals, mp 115–118°C (from 50% aqueous ethanol) after chromatography. (Found: C, 65.5; H, 5.5; N, 10.1, M 421.1677. $C_{23}H_{23}N_3O_5$ requires C, 65.5; H, 5.5; N, 10.0%, M 421.1638). $\nu_{max.}$ 1732, 1693, 1650, 1621, 1402, 1388, 1320, 1269 and 1024 cm^{-1}, δ_H (220 MHz) 12.40 (s, enol –OH), 8.12–7.23 (m, Ar*H*), 6.53 (m, Ar*H*), 5.25 (s, enol C3–*H*), 5.01 (d, *J*=9.5 Hz, keto C2–*H*), 4.21 (m, 2×enol –OCH_2CH$_3$, keto –OCH_2CH$_3$ and keto C3–*H*), 3.78 (m, keto –OCH_2CH$_3$), 2.30 (s, keto C4–CH_3), 2.24 (s, enol C4–CH_3), 1.31 (m, keto, –OCH_2CH$_3$ and enol –OCH_2CH$_3$), 1.11 (t, *J*=7.1 Hz, enol –OCH_2CH$_3$) and 0.55 (t, *J*=7.1 Hz, keto –OCH$_2$CH_3). The enol: keto ratio was determined to be 13:7 in $CDCl_3$ solution.

Method B. From diethyl fumarate **12** (R^2=Et): when diethyl maleate **11** (R^2=Et) was replaced with diethyl fumarate **12** (R^2=Et) in Method A above, compounds **14b/15b** (R^2=Et) (42%) were obtained after chromatography, identical with an authentic sample.

4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2-methoxycarbonylnaphth-1-ol 20a (R^2=Me). A mixture of compound **6a** (150 mg, 0.64 mmol), methyl acrylate (0.10 mL, 1.11 mmol) and benzene (5 mL) was heated (7 h) under reflux. The reaction mixture was allowed to cool to room temperature and evaporated. The residue was purified by chromatography (light petroleum bp 40–60°C: ethyl acetate, 3:1) giving compound **20** (R_f 0.59) (110 mg, 54%) as a colourless oil which crystallised upon standing. Recrystallisation from 70% aqueous ethanol gave white crystals, mp 106–108°C. (Found: C, 67.4; H, 4.9; N, 13.3, M 321.1108. $C_{18}H_{15}N_3O_3$ requires C, 67.3; H, 4.7; N, 13.1%, M 321.1113). $\nu_{max.}$ 1658, 1620, 1573, 1445, 1359, 1313 and 1273 cm^{-1}, δ_H (400 MHz) 12.48 (1H, s, –O*H*), 7.96 (1H, dd, *J*=7.5 and 1.3 Hz, Ar*H*), 7.86 (2H, m, Ar*H*), 7.44 (1H, dt, *J*=7.5 and 1.0 Hz, Ar*H*), 7.39 (2H, m, Ar*H*), 7.34 (1H, dt, *J*=7.5 and 1.3 Hz, Ar*H*), 6.73 (1H, d, *J*=7.5 Hz, Ar*H*), 6.24 (1H, dd, *J*=9.2 and 6.5 Hz, C4–*H*), 3.81 (3H, s, –OCH_3), 3.62 (1H, dd, *J*=15.8 and 9.2 Hz, C3–*H*) and 3.23 (1H, dd, *J*=15.8 and 6.5 Hz, C3–*H*).

4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2-methoxycarbonyl-4-methylnaphth-1-ol 20b (R^2=Me). Using a similar method to that described above for the preparation of compound **20a** (R^2=Me) but with a reflux period of 22 h, compound **6b** (200 mg, 0.8 mmol) and methyl acrylate (0.10 mL, 1.1 mmol) gave compound **20b** (R^2=Me) (175 mg, 65%) as white plates, mp 156–157°C (from 50% aqueous ethanol). (Found: C, 68.1; H, 5.3; N, 12.5, M 335.1285. $C_{19}H_{17}N_3O_3$ requires C, 68.1; H, 5.1; N, 12.5%, M 335.1269). $\nu_{max.}$ 1658, 1623, 1577, 1446, 1379, 1362, 1327, 1274 and 1263 cm^{-1}, δ_H (220 MHz) 12.83 (1H, s, –O*H*), 7.95 (1H, dd, *J*=7.6 and 1.9 Hz, Ar*H*), 7.88 (2H, m, Ar*H*), 7.38 (4H, m, Ar*H*), 6.71 (1H, dd, *J*=7.3 and 1.8 Hz, Ar*H*), 4.11 (1H, d, *J*=6.4 Hz, C3–*H*), 3.84 (3H, s, –OCH_3), 3.04 (1H, d, *J*=6.4 Hz, C3–*H*) and 2.21 (3H, s, C4–CH_3).

4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2-ethoxycarbonylnaphth-1-ol 20a (R^2=Et). Using a similar method to that described above for the preparation of compound **20a** (R^2=Me) but with a reflux period of 10 h, compound **6a** (1.0 g, 4.3 mmol) and ethyl acrylate (0.5 mL, 4.6 mmol) gave compound **20a** (R^2=Et) (1.37 g, 96%) as white needles, mp 112–113°C (from ethanol). (Found: C, 68.0; H, 5.0; N, 12.3, M 335.1275. $C_{19}H_{17}N_3O_3$ requires C, 68.1; H, 5.1; N, 12.5%, M 335.1270). $\nu_{max.}$ 1652, 1621, 1575, 1406, 1383, 1314, 1273 and 1084 cm^{-1}, δ_H (400 MHz) 12.56 (1H, s, –O*H*), 7.95 (1H, dd, *J*=7.8 and 1.4 Hz, Ar*H*), 7.88 (2H, m, Ar*H*), 7.40 (3H, m, Ar*H*), 7.32 (1H, dt, *J*=7.6 and 1.4 Hz, Ar*H*), 6.65 (1H, d, *J*=7.6 Hz, Ar*H*), 6.26 (1H, dd, *J*=10.2 and 6.6 Hz, C4–*H*), 4.27 (2H, m, –OCH_2CH$_3$), 3.60 (1H, dd, *J*=16.0 and 10.2 Hz, C3–*H*), 3.24 (1H, dd, *J*=16.0 and 6.6 Hz, C3–*H*) and 1.31 (3H, t, *J*=7.1 Hz, –OCH$_2$CH_3).

4-(2′H-Benzotriazol-2′-yl)-3,4-dihydro-2-ethoxycarbonyl-4-methylnaphth-1-ol 20b (R^2=Et). Using a similar method to that described above for the preparation of compound **20a** (R^2=Me) but with a reflux period of 30 h, compound **6b** (0.50 g, 2 mmol) and ethyl acrylate (0.25 mL, 2.3 mmol) gave compound **20b** (R^2=Et) (0.68 g, 97%) as a colourless oil which crystallised upon standing, mp 110–112°C (from 70% aqueous ethanol). (Found: C, 68.5; H, 5.5; N, 12.1, M 349.1432. $C_{20}H_{19}N_3O_3$ requires C, 68.8; H, 5.5; N, 12.0%, M 349.1427). $\nu_{max.}$1652, 1620, 1404, 1381, 1323, 1272 and 1262 cm^{-1}, δ_H (220 MHz) 12.53 (1H, s, –O*H*), 7.89 (3H, m, Ar*H*), 7.35 (4H, m, Ar*H*), 6.64 (1H, dd, *J*=7.7 and 1.2 Hz, Ar*H*), 4.31 (2H, q, *J*=7.1 Hz, –OCH_2CH$_3$), 4.11 (1H, d, *J*=15.7 Hz, C3–*H*), 3.05 (1H, d, *J*=15.7 Hz, C3–*H*), 2.21 (3H, s, C4–CH_3) and 1.34 (3H, t, *J*=7.1 Hz, –OCH$_2$CH_3).

(2α,4β)-4-(2′H-Benzotriazol-2′-yl)-2-ethoxycarbonyl-2-methyltetral-1-one 22a and (2α,4α)-4-(2′H-benzotriazol-2′-yl)-2-ethoxycarbonyl-2-methyltetral-1-one 23a. A mixture of compound **6a** (257 mg, 1.09 mmol), ethyl methacrylate **21** (0.16 mL, 1.28 mmol) and benzene (8 mL) was heated (26 h) at reflux with stirring. The reaction mixture was allowed to cool to room temperature and evaporated. The residue was purified by chromatography (light petroleum bp 40–60°C: ethyl acetate, 3:1) giving compound **22a** (R_f 0.65) (68 mg, 18%) as white needles mp 103–104°C (from 60% aqueous ethanol) and compound **23a** (R_f 0.52) (279 mg, 73%), mp 149–150°C (from ethanol). Compound **22a**: (Found: C, 68.5; H, 5.4; N, 12.4, M 349.1432. $C_{20}H_{19}N_3O_3$ requires C, 68.8; H, 5.5; N, 12.0%, M 349.1427), $\nu_{max.}$ 1739, 1695, 1602, 1455, 1327, 1294, 1181 and 1119 cm^{-1}, δ (220 MHz) 8.17 (1H, m, Ar*H*), 7.90 (2H, m, Ar*H*), 7.43 (4H, m, Ar*H*), 6.63 (1H, dd, X part of ABX system, *J*=10.6 and 5.0 Hz, C4–*H*), 6.56 (1H, m, Ar*H*), 4.21 (2H, q, *J*=7.2 Hz, –OCH_2CH$_3$), 3.12 (2H, AB part of ABX system, δ_A 3.12 and δ_B 3.10, *J*=13.2, 10.6 and 5.0 Hz, C3–H_2), 1.64 (3H, s, C2–CH_3) and 1.18 (3H, t, *J*=7.2 Hz, –OCH_2CH$_3$). Compound **23a**: (Found: C, 68.7; H, 5.4; N, 12.3, M 349.1429. $C_{20}H_{19}N_3O_3$ requires C, 68.8; H, 5.5; N, 12.0%, M 349.1426), $\nu_{max.}$ 1738, 1692, 1326, 1270, 1255 and 1113 cm^{-1}, δ_H (220 MHz) 8.18 (1H, m, Ar*H*), 7.92 (2H, m, Ar*H*), 7.47 (4H, m, Ar*H*), 6.58 (1H, m, Ar*H*), 6.49 (1H, dd, *J*=12.2 and 5.3 Hz, C4–*H*), 4.21 (2H, m, –OCH_2CH$_3$), 3.79 (1H, dd, *J*=13.3 and 12.2 Hz, C3–*H*), 2.62 (1H, dd, *J*=13.3 and 5.3 Hz, C3–*H*), 1.67 (3H, s, C2–CH_3), 1.23 (3H, t, *J*=7.2 Hz, –OCH$_2$CH_3).

(2α,4β)-4-(2′H-Benzotriazol-2′-yl)-2-ethoxycarbonyl-2,4-dimethyltetral-1-one 22b and (2α,4α)-4-(2′H-benzotriazol-2′-yl)-2-ethoxycarbonyl-2,4-dimethyltetral-1-one 23b. Using a similar method to that described above for the preparation of compounds **22a** and **23a**, compound **6b** (218 mg, 0.88 mmol) and ethyl methacrylate (0.13 mL, 1.04 mmol) in benzene (7 mL) at reflux (54 h) gave compound **22b** (R_f 0.53) (47 mg, 15%), mp 111–112°C (from 60% aqueous ethanol) and compound **23b** (R_f 0.34, 216 mg, 69%), mp 129–132°C (from 95% aqueous ethanol). Compound **22b**: (Found: C, 69.3; H, 5.6; N, 11.6, M 363.1554. $C_{21}H_{21}N_3O_3$ requires C, 69.4; H, 5.8; N, 11.6%, M 363.1582), $\nu_{max.}$ 1728, 1693, 1601, 1458, 1321, 1251 and 1130 cm^{-1}, δ_H (220 MHz) 8.21 (1H, m, Ar*H*), 7.87 (2H, m, Ar*H*), 7.42 (4H, m, Ar*H*), 6.82 (1H, m, Ar*H*), 4.22 (2H, q, *J*=7.2 Hz, –OCH_2CH$_3$), 3.48 (1H, d, *J*=14.3 Hz, C3–*H*), 3.07 (1H, d, *J*=14.3 Hz, C3–*H*), 2.28 (3H, s, C4–CH_3), 1.44 (3H, s, C2–CH_3) and 1.22 (3H, t, *J*=7.2 Hz, –OCH_2CH$_3$). Compound **23b**: (Found: C, 69.1; H, 5.8; N, 11.8, M 363.1575. $C_{21}H_{21}N_3O_3$ requires C, 69.4; H, 5.8; N, 11.6%, M 363.1582), $\nu_{max.}$ 1732, 1696, 1602, 1458, 1325, 1255, 102 and 926 cm^{-1}, δ_H (220 MHz) 8.23 (1H, dd, *J*=8.8 and 1.6 Hz, Ar*H*), 7.78 (2H, m, Ar*H*), 7.64 (1H, dt, *J*=8.8 and 1.6 Hz, Ar*H*), 7.54 (1H, dt, *J*=8.8 and 1.2 Hz, Ar*H*), 7.46 (1H, dd, *J*=8.8 and 1.2 Hz, Ar*H*), 7.31 (2H, m Ar*H*), 3.68 (1H, d, *J*=14.4 Hz, C3–*H*), 3.25 (2H, m, –OCH_2CH$_3$), 2.51 (1H, d, *J*=14.4 Hz, C3–*H*), 2.26 (3H, s, C4–CH_3), 1.49 (3H, s, C2–CH_3) and 0.72 (3H, t, *J*=7.2 Hz, –OCH$_2$CH_3).

4-(2′H-Benzotriazol-2′-yl)-2-cyano-4-methyl-1-oxo-1,4-dihydronaphthalene 26b. A mixture of compound **6b** (300 mg, 1.2 mmol), acrylonitrile (0.1 mL, 1.5 mmol) and benzene (10 mL) was heated at reflux (30 h) with stirring. The reaction mixture was allowed to cool to room temperature, evaporated and triturated with methanol giving a white solid (198 mg) which was shown to be a mixture of diastereoisomers by ^{1}H NMR spectroscopy. Attempts to separate this mixture of products by chromatography resulted in decomposition. These products, benzene (5 mL) and DDQ (151 mg, 0.67 mmol) were heated (2 h) at reflux, the mixture was filtered whilst hot, the filtrate was allowed to cool to room temperature and evaporated. The residue was triturated with ethanol (5 mL) giving compound

26b (95 mg, 26%), mp 230–232°C (from ethanol). (Found:, C, 71.8; H, 4.4; N, 19.0, M 300.1007. $C_{18}H_{12}N_4O$ requires C, 72.0; H, 4.0; N, 18.7%, M 300.1011). $\nu_{max.}$ 2339, 1684, 1603, 1459, 1364, 1320, 1253, 1079 and 974 cm^{-1}, δ_H (220 MHz) 8.26 (1H, dd, *J*=8.4 and 2.0 Hz, Ar*H*), 7.89 (3H, m, Ar*H*), 7.50 (5H, m, C3–*H* and Ar*H*) and 2.47 (3H, s, $-CH_3$).

2,3-Diethoxycarbonylnaphth-1-yl acetate 27a. A mixture of compound **18a** (R^2=Et) (191 mg, 0.5 mmol), acetic anhydride (1.0 mL) and pyridine (0.2 mL) was heated (2 h) at reflux. The mixture was allowed to cool to room temperature, poured into water (10 mL) and extracted with chloroform (3×7 mL). The combined organic extracts were washed with water (10 mL), dried ($MgSO_4$) and evaporated. The residue was purified by chromatography (light petroleum bp 40–60°C: ethyl acetate, 3:1) giving a mixture (R_f 0.73) of 1-acetylbenzotriazole and benzotriazole by ^1H NMR spectroscopy and compound **27a** (R_f 0.37) (130 mg, 84%) as white crystals, mp 90–91°C (from benzene–hexane). (Found: C, 65.7; H, 5.6, M 330.1118. $C_{18}H_{18}O_6$ requires C, 65.5; H, 5.5%, M 330.1103). $\nu_{max.}$ 1775, 1722, 1448, 1368, 1276, 1180, 142, 1079 and 1032 cm^{-1}, δ_H (220 MHz) 8.41 (1H, s, C4–*H*), 7.94 (1H, dd, *J*=7.0 and 2.0 Hz, Ar*H*), 7.82 (1H, dd, *J*=7.0 and 1.8 Hz, Ar*H*), 7.60 (2H, m, Ar*H*), 4.42 (4H, 2×q, *J*=7.3 and 7.3 Hz, 2×–OCH_2CH_3), 2.42 (3H, s, $-OCOCH_3$) and 1.38 (6H, t, *J*=7.3 Hz, 2×– OCH_2CH_3).

4-(2′H-Benzotriazol-2′-yl)-2-ethoxycarbonyl-3,4-dihydronaphth-1-yl acetate 28a. A mixture of compound **20a** (R^2=Et) (200 mg, 0.6 mmol), acetic anhydride (2 mL) and pyridine (0.5 mL) was heated (2 h) under reflux. The reaction mixture was allowed to cool to room temperature and added to water (20 mL). The mixture was extracted with chloroform (3×10 mL) and the combined organic extracts were washed with water (10 mL), dried ($MgSO_4$) and evaporated. The residual oil was triturated with ethanol giving compound **28a** (129 mg, 57%) as white crystals, mp 111–113°C. (Found: C, 66.6; H, 5.3; N, 11.1, M 377.1377. $C_{21}H_{19}N_3O_4$ requires C, 66.8; H, 5.1; N, 11.1%, M 377.1376), $\nu_{max.}$ 1771, 1707, 1639, 1372, 1189, 1139 and 1075 cm^{-1}, δ_H (220 MHz) 7.89 (2H, m, Ar*H*), 7.48 (1H, dd, *J*=7.3 and 2.2 Hz, Ar*H*), 7.35 (4H, m, Ar*H*), 6.70 (1H, d, *J*=7.1 Hz, Ar*H*), 6.37 (1H, dd, *J*=11.0 and 7.3 Hz, C4–*H*), 4.23 (2H, q, *J*=6.9 Hz, $-OCH_2CH_3$), 3.84 (1H, dd, *J*=17.1 and 11.0 Hz, C3–*H*), 3.39 (1H, dd, *J*=17.1 and 7.3 Hz, C3–*H*), 2.39 (3H, s, $-OCOCH_3$) and 1.28 (3H, t, *J*=6.9 Hz, $-OCH_2CH_3$).

4-(2′H-Benzotriazol-2′-yl)-2-ethoxycarbonyl-3,4-dihydro-4-methylnaphth-1-yl acetate 28b. Using a similar method to that described above, compound **20b** (R^2=Et) (200 mg, 0.57 mmol), acetic anhydride (4 mL) and pyridine (1 mL) gave compound **28b** (170 mg, 76%), mp 133–134°C (from ethanol). (Found: C, 67.3; H, 5.5; N, 10.6, M 391.1552. $C_{22}H_{21}N_3O_4$ requires C, 67.5; H, 5.4; N, 10.7%, M 391.1532), $\nu_{max.}$ 1769, 1708, 1640, 1382, 1305, 1254, 1190, 1139 and 1068 cm^{-1}, δ_H (220 MHz) 7.90 (2H, m, Ar*H*), 7.38 (5H, m, Ar*H*), 6.58 (1H, d, *J*=7.0 Hz, Ar*H*), 4.28 (3H, m, C3–*H* and $-OCH_2CH_3$), 3.22 (1H, d, *J*=16.8 Hz, C3–*H*), 2.39 (3H, s, $-OCOCH_3$), 2.28 (3H, s, C4–CH_3) and 1.31 (3H, t, *J*=7.0 Hz, $-OCH_2CH_3$).

Diethyl 1-hydroxy-2,3-naphthalene dicarboxylate 29a. A mixture of compound **14a** (R^2=Et) (269 mg, 0.66 mmol), DBN (1 drop) and benzene (5 mL) was heated (0.5 h) at reflux. The reaction mixture was allowed to cool to room temperature and evaporated. The residue was purified by chromatography (light petroleum bp 40–60°C: ethyl acetate, 3:1) giving compound **29a** (R_f 0.71) (130 mg, 68%) as white needles, mp 53–54°C (from ethanol) (lit.[8] mp 52–54°C) and benzotriazole (R_f 0.16) (50 mg, 64%), identical with an authentic sample.

Diethyl 1-hydroxy-4-methyl-2,3-naphthalene dicarboxylate 29b. Using a similar method to that described above, compound **14b** (R^2=Et) (199 mg, 0.47 mmol), DBN (2 drops) and benzene (3 mL) at reflux (5.5 h) gave compound **29b** (R_f 0.61) (110 mg, 77%) as white needles, mp 79–81°C (from ethanol) and benzotriazole (R_f 0.12) (39 mg, 69%), identical with an authentic sample. Compound **29b**: (Found: C, 67.5; H, 6.0, M 302.1164. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%, M 302.1155), $\nu_{max.}$ 1728, 1659, 1585, 1410, 1378, 1333, 1109, 1059 and 1025 cm^{-1}, δ_H (220 MHz) 12.48 (1H, s, –O*H*), 8.47 (1H, dd, *J*=8.0 and 1.2 Hz, Ar*H*), 7.96 (1H, dd, *J*=8.4 and 1.2 Hz, Ar*H*), 7.68 (1H, dt, *J*=8.4, 6.9 and 1.2 Hz, Ar*H*), 7.56 (1H, dt, *J*=8.0, 6.9 and 1.2 Hz, Ar*H*), 4.44 (4H, m, 2×–OCH_2CH_3), 2.49 (3H, s, C4-CH_3) and 1.40 (6H, m, 2×–OCH_2CH_3).

4-(2′H-Benzotriazol-2′-yl)tetral-1-one 30a. A mixture of compound **20a** (R^2=Et) (1.0 g, 3 mmol) and dilute sodium hydroxide solution (2 M, 30 mL) was heated under reflux (6.5 h) with stirring. The reaction mixture was allowed to cool to room temperature, acidified with dilute hydrochloric acid and then extracted with chloroform (3×40 mL). The combined chloroform extracts were dried ($MgSO_4$) and evaporated giving compound **30a** (0.69 g, 88%) as white needles, mp 157–159°C (from ethanol). (Found: C, 72.9; H, 5.2; N, 15.8, M 263.1062. $C_{16}H_{13}N_3O$ requires C, 73.0; H, 5.0; N, 16.0%, M 263.1059). $\nu_{max.}$ 1693, 1603, 1458, 1330 and 1292 cm^{-1}, δ_H (400 MHz) 8.16 (1H, m, Ar*H*), 7.88 (2H, m, Ar*H*), 7.48 (2H, m, Ar*H*), 7.41 (2H, m, Ar*H*), 6.89 (1H, m, Ar*H*), 6.37 (1H, dd, *J*=8.1 and 4.3 Hz, C4–*H*), 3.13 (1H, m, C2–*H*), 3.03 (1H, m, C3–*H*) and 2.79 (2H, m, C2–*H* and C3–*H*).

4-(2′H-Benzotriazol-2′-yl)-4-methyltetral-1-one 30b. Using a similar method to that described above for the preparation of compound **30a**, compound **20b** (R^2=Et) (200 mg, 0.58 mmol) gave compound **30b** (125 mg, 56%), mp 174–175°C (from ethanol). (Found: C, 73.4; H, 5.7; N, 14.9, M 277.1228. $C_{17}H_{15}N_3O$ requires C, 73.6; H, 5.5; N, 15.2%, M 277.1215), $\nu_{max.}$ 1691, 1605, 1458, 1333 and 1292 cm^{-1}, δ_H (400 MHz) 8.13 (1H, dd, *J*=7.9 and 1.9 Hz, Ar*H*), 7.86 (2H, m, Ar*H*), 7.51 (1H, dt, *J*=7.9 and 1.9 Hz, Ar*H*), 7.45 (1H, dt, *J*=7.9 and 1.3 Hz, Ar*H*), 7.38 (2H, m, Ar*H*), 7.05 (1H, dd, *J*=7.9 and 1.3 Hz, Ar*H*), 3.41 (1H, m, C3–*H*), 2.85 (2H, m, C2–H_2), 2.55 (1H, m, C3–*H*) and 2.34 (3H, s, $-CH_3$).

4-(2′H-Benzotriazol-2′-yl)tetral-1-one 30a, ethyl 1-hydroxy-2-naphthoate 31a and benzotriazole. A mixture of compound **20a** (R^2=Et) (218 mg, 0.65 mmol), ethanol (5 mL) and dilute hydrochloric acid (2 M, 5 mL) was heated under reflux (5 h) with stirring. The reaction mixture was

allowed to cool to room temperature and extracted with chloroform (3×7 mL). The combined organic extracts were dried ($MgSO_4$), evaporated and the residue was purified by chromatography (petroleum ether bp 40–60°C: ethyl acetate, 3:1) giving compound **31a** (R_f 0.88) (43 mg, 31%) as a colourless oil which crystallised upon standing, mp 48–49°C (from ethanol) (lit.[9] mp 49°C), compound **30a** (R_f 0.49) (70 mg, 41%) and benzotriazole (R_f 0.15) (20 mg, 26%), both identical authentic samples.

Ethyl 1-hydroxy-4-methyl-2-naphthoate 31b and benzotriazole. In a similar manner to that described above for the acidic hydrolysis of compound **20a** (R^2=Et), compound **20b** (R^2=Et) (227 mg, 0.9 mmol) gave compound **31b** (R_f 0.88) (86 mg, 58%) as white needles, mp 85–86°C (from ethanol) and benzotriazole (50 mg, 65%), identical with an authentic sample. Compound **31b**: (Found: C, 73.0; H, 6.2, M 230.0937. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1%, M 230.0943), $\nu_{max.}$ 1662, 1646, 1588, 1409, 1375, 1340, 1248, 1158, 1100 and 1023 cm^{-1}, δ_H (220 MHz) 11.88 (1H, s, –O*H*), 8.43 (1H, d, *J*=8.0 Hz, Ar*H*), 7.84 (1H, d, *J*=7.8 Hz, Ar*H*), 7.55 (3H, m, Ar*H*), 4.42 (2H, q, *J*=7.1 Hz, $-OCH_2CH_3$), 2.52 (3H, s, C4–CH_3) and 1.42 (3H, t, *J*=7.1 Hz, $-OCH_2CH_3$).

4-(2′H-Benzotriazol-2′-yl)-2-ethoxycarbonylnaphth-1-ol 32. A mixture of compound **20a** (R^2=Et) (178 mg, 0.53 mmol), DDQ (122 mg, 0.54 mmol) and benzene (5 mL) was heated (24 h) at reflux with stirring. The reaction was filtered whilst hot and the filtrate was allowed to cool to room temperature and then evaporated. The residue was triturated with ethanol giving compound **32** (150 mg, 85%), mp 144–145°C (from ethanol). (Found: C, 68.2; H, 4.8; N, 12.7, M 333.1118. $C_{19}H_{15}N_3O_3$ requires C, 68.5; H, 4.5; N, 12.6%, M 333.1114), $\nu_{max.}$ 1657, 1640, 1398, 1377, 1319, 1240 and 1098 cm^{-1}, δ_H (220 MHz) 12.36 (1H, s, –O*H*), 8.55 (1H, dd, *J*=7.8 and 1.6 Hz, Ar*H*), 8.29 (1H, s, C3–*H*), 8.05 (3H, m, Ar*H*), 7.67 (2H, m, Ar*H*), 7.49 (2H, m, Ar*H*), 4.50 (2H, q, *J*=7.3 Hz, $-OCH_2CH_3$) and 1.42 (3H, q, *J*=7.3 Hz, $-OCH_2CH_3$).

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