PERKIN 1

Neighboring group effect of pyridazine and pyrazine rings for π-facial selectivity in the reactions of fused isopropylidene-norbornene systems with electrophilic reagents

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A series of pyridazine- and pyrazine-fused isopropylidenenorbornenes† have been synthesized and the π-facial selectivity of the electrophilic reactions with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (PTAD), *m*-chloroperbenzoic acid (MCPBA) and *N*-bromosuccinimide (NBS) has been investigated. The ene reactions with PTAD exhibited exclusive *syn* selectivity to the heteroaromatic rings except for an isopropylidenenorbornene fused with a pyridazine *N*-oxide ring. The epoxidations with MCPBA and the ene reactions with NBS afforded mixtures of *syn* and *anti* isomers depending on the heteroaromatic rings and substituents. The predominant *syn* selectivity compared with that of a benzene-fused congener may be attributed to the presence of a strong positive electrostatic potential field over the heteroaromatic ring to stabilize a polar transition state by the electrostatic interaction.

Introduction

A large number of experimental and theoretical studies on π-facial stereoselectivity have been reported.[1–9] In particular, the π-facial selectivity in reactions of 7-isopropylidene-norbornene[10–14] **1** and benzene-fused 7-isopropylidenenorborn-ene[15–17] **2** has been investigated in detail. However, essentially no attention has been paid to the possible control of π-facial selectivity by a neighboring heteroaromatic ring. Recently, we reported that even the electron-deficient six-membered hetero-aromatic rings such as pyridazine and pyrazine effected the stabilization of a remote cationic center to some extent,[17–19] and that five-membered heteroaromatics were more effective for stabilization than was a benzene ring.[20,21] The results inspired us to investigate the neighboring effect of six-membered hetero-aromatic rings for π-facial selectivity in the electrophilic reac-tions of fused isopropylidenenorbornene systems, in due course. In this paper we describe the syntheses and the electro-philic reactions of the pyridazine-fused isopropylidene-norbornadienes **3**–**5** and isopropylidenenorbornenes **6**–**8**, as well as of the pyrazine-fused isopropylidenenorbornadienes **9**–**12** and isopropylidenenorbornenes **13**–**16** (see Chart 1).

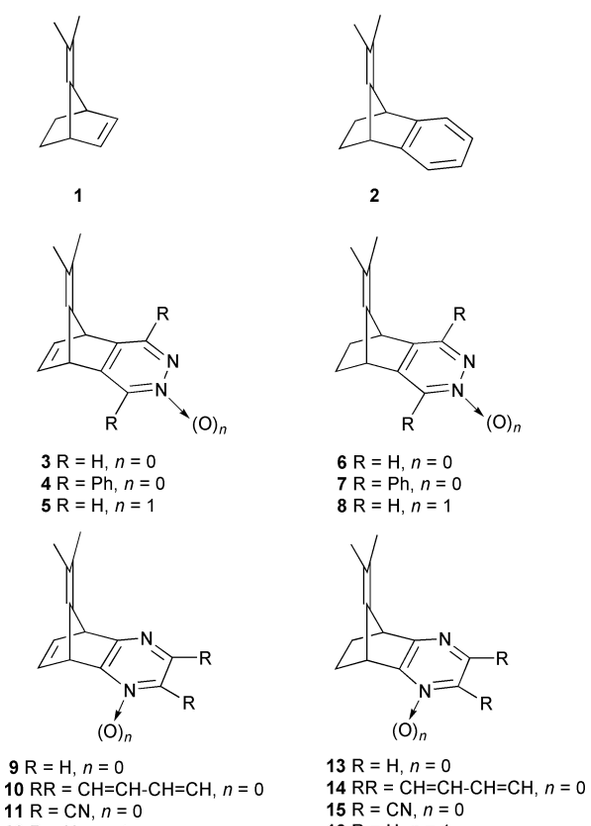

Chart 1

Results and discussion

Syntheses of fused isopropylidenenorbornene derivatives

Cycloaddition reaction of 4,4-diethoxybut-2-ynal **17** with 6,6-dimethylfulvene **18** in refluxing toluene gave the adduct **19** (Scheme 1). Attempted distillation of **19** resulted in its decom-position and we used **19** for the next step without further purifi-cation. Hydrolysis of **19** with formic acid and subsequent one-pot treatment with hydrazine hydrate provided the pyridazine-fused isopropylidenenorbornadiene **3** in 40% overall yield from **17**. Hydrogenation of **3** with Pd/C resulted in selective reduction of the endocyclic double bond to give the pyridazine-fused isopropylidenenorbornene **6**. The diphenyl-substituted pyridazine **4** was similarly prepared by the reaction of hydrazine hydrate and **21**, which was obtained by the Diels–Alder reaction of dibenzoylacetylene **20** and the fulvene **18**.

Since the hydrogenation of **4** afforded a mixture of products, the diphenylpyridazine-fused isopropylidenenorbornene **7** was prepared by hydrogenation of **21** followed by treatment with hydrazine hydrate. The pyridazine *N*-oxide **5** was obtained by oxidation of **3** with *m*-chloroperbenzoic acid (MCPBA). Hydrogenation of **5** successfully afforded **8**, whereas the MCPBA oxidation of **6** resulted in the formation of a mixture of products.

† The IUPAC name for norbornene is bicyclo[2.2.1]heptene.

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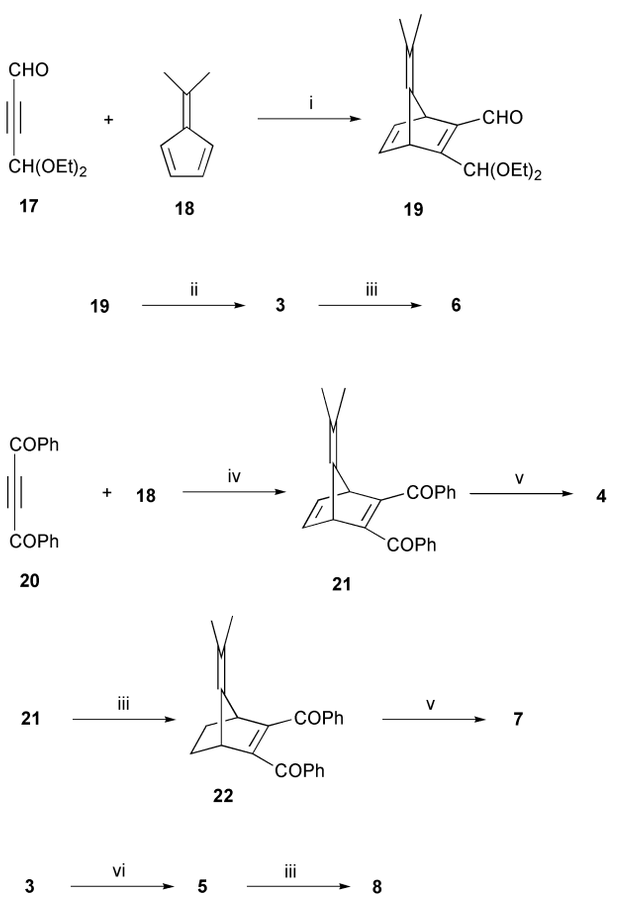
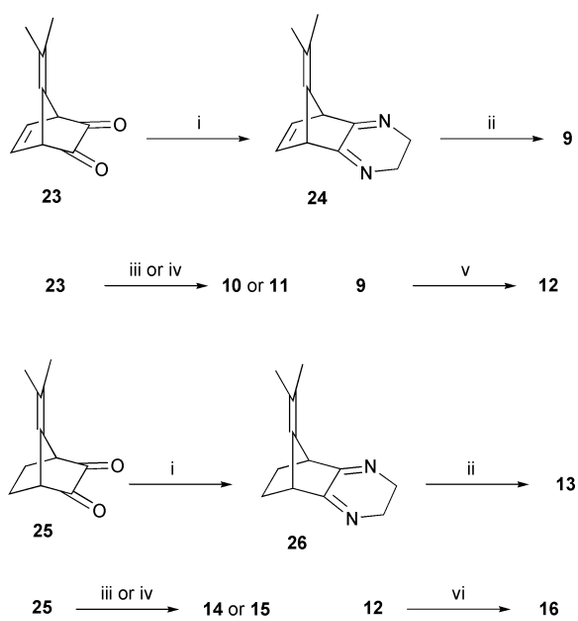
Table 1 Products and ratios of *syn* and *anti* isomers in the electrophilic reactions of fused isopropylidenenorbornenes

Substrate	Electrophiles		
	PTAD (*syn* : *anti*)	MCPBA (*syn* : *anti*)	NBS (*syn* : *anti*)
3	**27** (100 : 0)	**5**	recovery
4	**28** (100 : 0)		
5	**29** (100 : 0)	**42** and **43** (73 : 27)	recovery
6	**34** (100 : 0)	**8**	**58** and **59** (44 : 56)
7	**35** (100 : 0)		
8	**36** and **37** (91 : 9)	**48** and **49** (46 : 54)	**60** and **61** (28 : 72)
9	**30** (100 : 0)	**12**	complex
10	**31** (100 : 0)	**44** (100 : 0) and **45**	
11	**32** (100 : 0)	**46** (100 : 0)	recovery
12	**33** (100 : 0)	**47** (100 : 0)	complex
13	**38** (100 : 0)	**50** and **51** (40 : 60)	**62** and **63** (34 : 66)
14	**39** (100 : 0)	**52** and **53** (37 : 63)	**64** and **65** (30 : 70)
15	**40** (100 : 0)	**54** and **55** (83 : 17)	**66** and **67** (71 : 29)
16	**41** (100 : 0)	**56** and **57** (45 : 55)	complex
2[14]	19 : 81[a]	17 : 83	19 : 81
2-Cl_4[14]	59 : 41[a]	31 : 69	58 : 42

[a] Reaction with 4-methyl-1,2,4-triazole-3,5(4*H*)-dione.[14]



Scheme 1 *Reagents and conditions*: i, Toluene, reflux; ii (a) HCOOH, $CHCl_3$, reflux (b) $NH_2NH_2{\cdot}H_2O$, reflux; iii, H_2, Pd/c, AcOEt, EtOH (2 : 1), rt; iv, benzene, reflux; v, $NH_2NH_2{\cdot}H_2O$, EtOH, CH_3COOH, H_2O, reflux; vi, MCPBA, CH_2Cl_2, rt.



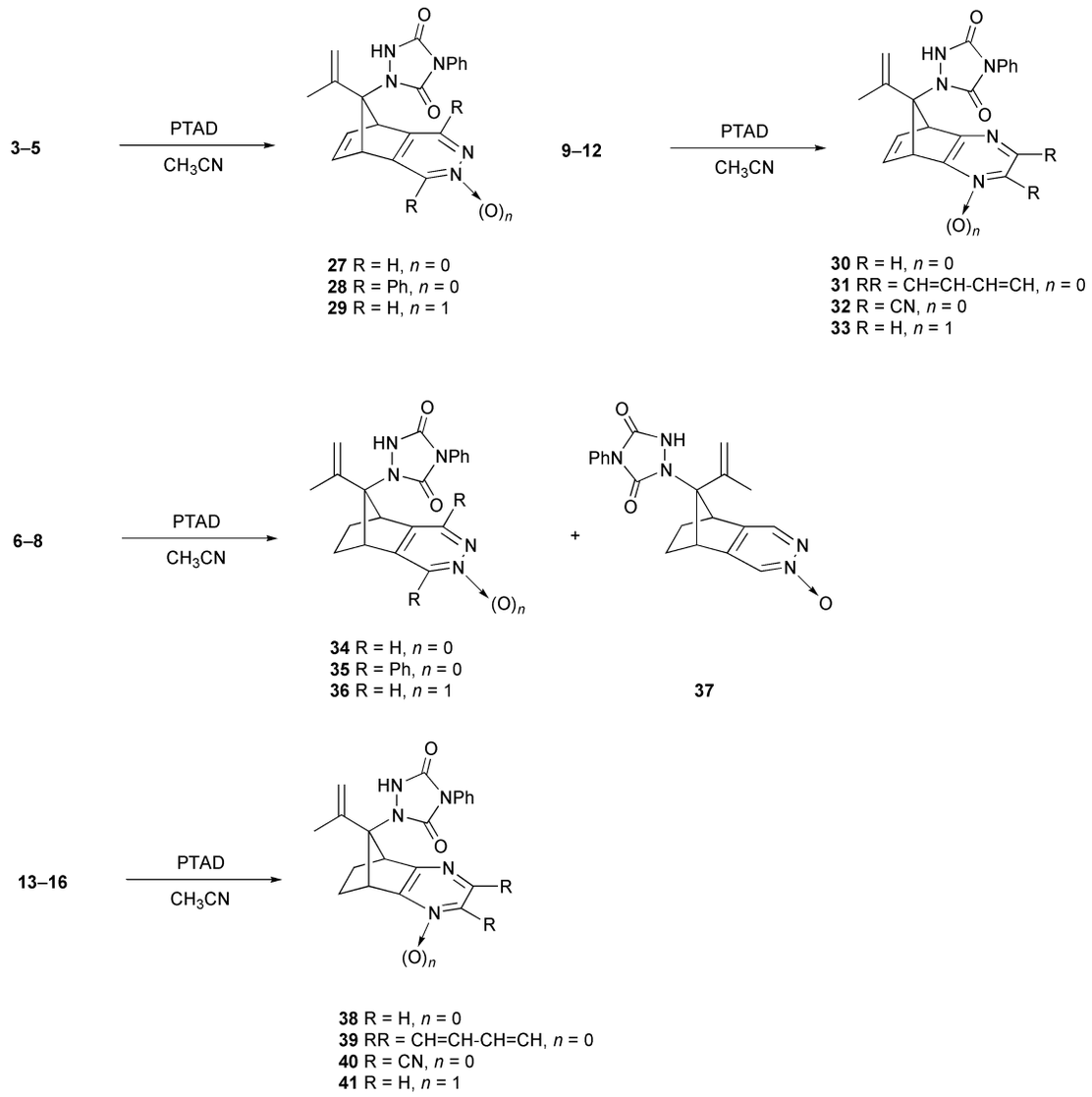
Scheme 2 *Reagents and conditions*: i, $NH_2CH_2NH_2$, *p*-TsOH, benzene, reflux; ii, nickel peroxide, benzene, reflux; iii, *o*-phenylenediamine, CH_3COOH, reflux; iv, diaminomaleonitrile, THF, reflux; v, MCPBA, CH_2Cl_2, rt; vi, H_2, Pd/c, AcOEt, rt.

The pyrazine-fused isopropylidenenorbornadiene **9** was prepared by the reaction of 7-isopropylidenebicyclo[2.2.1]-hept-5-ene-2,3-dione[22] **23** with ethylenediamine, followed by dehydrogenation with nickel peroxide (Scheme 2). Oxidation of **9** with MCPBA gave the corresponding pyrazine *N*-oxide **12**. Condensation reactions of **23** with *o*-phenylenediamine or diaminomaleonitrile respectively provided the fused quinoxaline **10** or the dicyanopyrazine **11**. Pyrazine-fused isopropylidenenorbornenes were similarly prepared by the use of 7-isopropylidenebicyclo[2.2.1]heptane-2,3-dione[23] **25** as the starting diketone: treatment of **25** with ethylenediamine followed by dehydrogenation afforded **13**, and the condensation reactions with *o*-phenylenediamine and diaminomaleonitrile gave **14** and **15**, respectively. The pyrazine *N*-oxide **16** was prepared by the hydrogenation of **12**.

Electrophilic reactions of pyridazine- and pyrazine-fused isopropylidenenorbornene derivatives

Electrophilic reactions of the pyridazine- and pyrazine-fused isopropylidenenorbornene derivatives with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (PTAD), MCPBA, and *N*-bromosuccinimide (NBS) were investigated. The ratios of *syn* and *anti* isomers of the products in these reactions are summarized in Table 1.

On treatment with PTAD at room temperature in acetonitrile, the pyridazine- and pyrazine-fused isopropylidene-



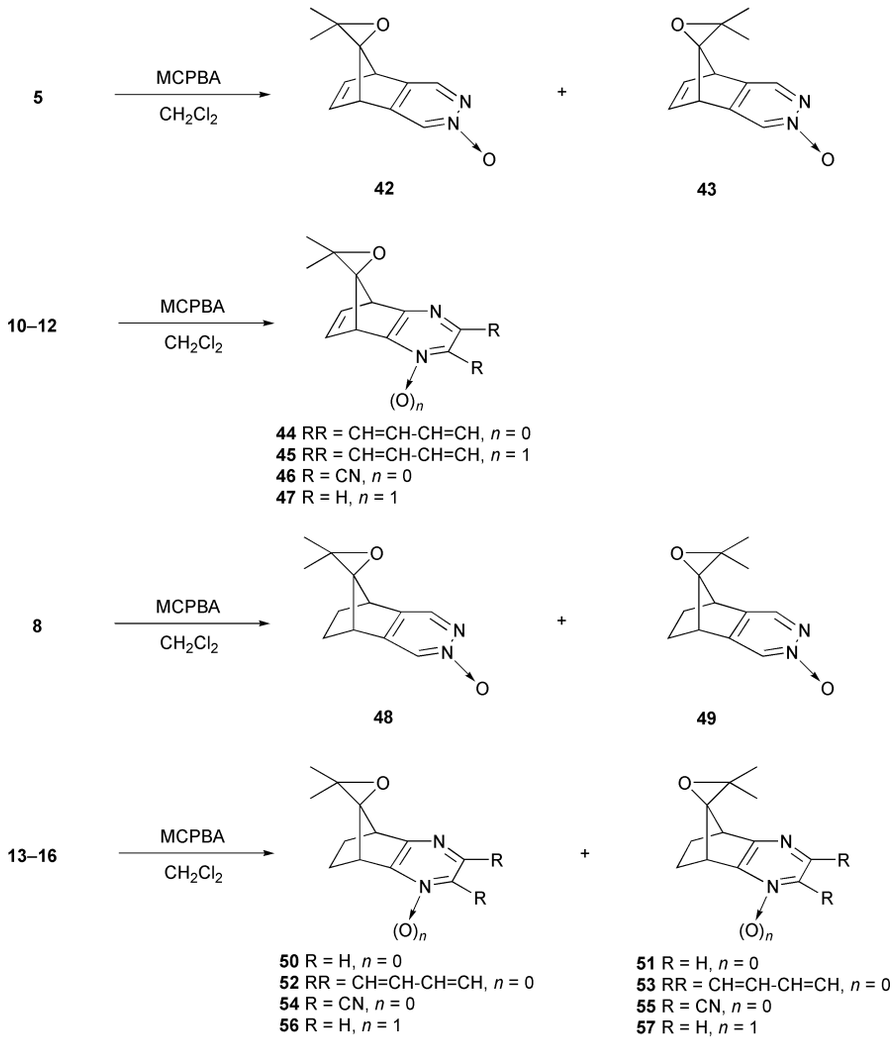
Scheme 3

norbornadienes **3**–**5** and **9**–**12** provided the ene-reaction products **27**–**33**, where PTAD attacks exclusively from the *syn* face with respect to the heteroaromatic rings (Scheme 3). The yields of the products were 90–99% and we could observe no evidence for the formation of *anti* isomers. Although 9-isopropylidene-5,8-dihydro-5,8-methanonaphthalene (isopropylidenebenzonorbornadiene) was reported to give a single ene-reaction product on treatment with PTAD, the stereochemistry was ambiguous.[14,24] In contrast, the stereochemistry of all the ene-reaction products **27**–**33** was clearly determined as being *syn* by the observations of NOEs between the methyl group and the olefinic protons at C-6 and C-7. The X-ray crystallographic analysis of **27** also confirmed the *syn* configuration of the product (Fig. 1).

The exclusive *syn* preference of these reactions is assumed to be due to the existence of the endocyclic double bond which would stabilize a transition state of the reaction by bishomoaromatic interaction of π-systems.[11,14,25–30] However, the reactions of fused isopropylidenenorbornenes **6**–**8** and **13**–**16** with PTAD, where the endocyclic double bonds potentially involved in such bishomoaromatic stabilization are absent, resulted in the formation of only *syn* products **34**, **35**, and **38**–**41** except for the case of the pyridazine *N*-oxide **8**. The results are in contrast to that of isopropylidenebenzonorbornene **2** with 4-methyl-1,2,4-triazole-3,5(4*H*)-dione, where a mixture of *syn* and *anti* isomers was obtained in a ratio of 19 : 81 with *anti* preference (Table 1).[14] The reaction of the pyridazine *N*-oxide **8** with PTAD afforded a mixture of the *syn* and *anti* isomers **36** and **37** in a ratio of 91 : 9 probably due to the electron-donating effect of the *N*-oxide group. However, such an effect was not observed in the reaction of the fused pyrazine *N*-oxide **16** with PTAD.

The stereochemistry of **34**, **35**, and **38**–**41** was determined by the observation of NOEs between the methyl group and 5-*exo* and 6-*exo* protons by NOE differential spectroscopy. On the other hand, the stereochemistry of an inseparable mixture of **36** and **37** was deduced from the ^{1}H-NMR spectral data. Table 2 shows the assignment of the ^{1}H chemical shifts for **36** and **37** as well as those of **34**. The chemical shifts for the *syn* isomer **36** seem to be similar to those of **34**. In contrast, the methyl and methylene protons on the isopropenyl group of the *anti* isomer **37** are rather shielded when compared with those of **36**, probably due to the shielding effect of the pyridazine ring. The deshielding of 6-H_{exo} and 7-H_{exo} protons of **37** also supported the *anti* configuration of **37**.

The oxidation reactions of the isopropylidenenorbornadiene fused with a pyridazine *N*-oxide, compound **5**, with MCPBA gave a mixture of *syn* and *anti* epoxides **42** and **43** in a ratio of 73 : 27 (Scheme 4). On the other hand, MCPBA oxidation of the fused isopropylidenenorbornene **8** afforded predominant *anti* attack to give *syn* and *anti* isomers **48** and **49** with a ratio of 46 : 54. The presence of an endocyclic double bond was found to be effective for the formation of a *syn* iso-



Scheme 4

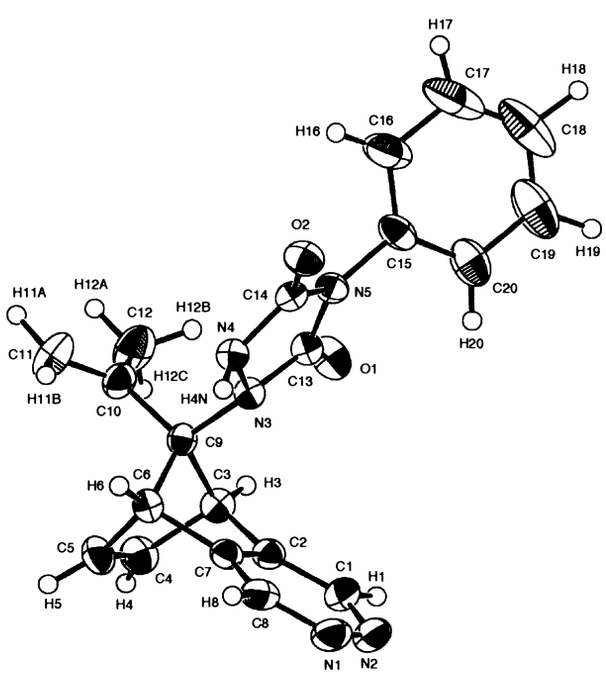


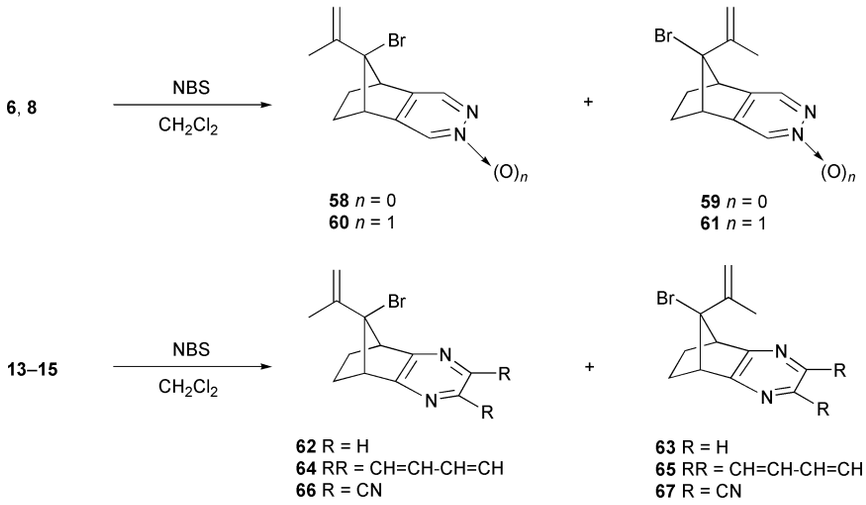
Fig. 1 ORTEP plot of **27**, with crystallographic numbering scheme. Atoms are drawn at the 50% probability level of electron density.

mer. The quinoxaline-fused derivative **10** provided only *syn* epoxide **44** along with its *N*-oxide **45**. The dicyanopyrazine **11** and the pyrazine *N*-oxide **12** also gave only *syn* epoxides **46** and **47**, respectively. The pyrazine-fused isopropylidenenorbornenes **13**–**16** gave mixtures of *syn* and *anti* epoxides. Epoxidation of the dicyanopyrazine **15** exhibited a strong *syn* preference, and the ratios of *syn* isomers seem to increase in the order of **14** < **13** < **16** < **15**. The *N*-oxide group of the fused pyrazine **16** was not effective in promoting the formation of the *anti* isomer **57**, as similarly recognized in the reactions with PTAD.

Table 2 ^{1}H-NMR data [δ(ppm)] of selected ene-reaction products **34**, **36**, and **37**

Assignment	**34**	**36**	**37**
6-H_{endo} and 7-H_{endo}	1.17	1.30	1.31
CH_3	1.87	1.87	*1.64*
6-H_{exo} and 7-H_{exo}	2.08	2.07	*2.41*
5-H and 8-H	4.27	4.24	4.23
$=CH_2$	5.22, 5.24	5.19, 5.24	*4.97*
1-H and 4-H	9.20	8.22, 8.35	8.35, 8.42

The reactions of fused isopropylidenenorbornadiene derivatives **3**–**5** and **9**–**12** with NBS resulted in the recovery of starting materials or the formation of complex products. The pyridazine-fused isopropylidenenorbornenes **6** and **8** provided ene-reaction products, where introduction of the *N*-oxide group was found to increase the relative amount of *anti* product (see Scheme 5). For the reactions of pyrazine-fused isopropylidenenorbornenes **13**–**15**, the ratios for the formations of *syn* isomers increased in the order of **14** < **13** < **15**, in good agreement with that observed for the epoxidation of these compounds.



Scheme 5

Previously, the π-facial selectivity for isopropylidenenorbornene **1** and its benzene-fused congener **2** was variously understood in terms of a steric effect, homoaromatic charge distribution and electrostatic interaction.[10,12,14] However, Houk and co-workers have recently reported that the π-facial stereochemical variations of these compounds can be attributed simply to electrostatic effects.[16]

We calculated the electrostatic potential fields of fused pyridazines and pyrazines by the PM3-MNDO method.[31] Fig. 2 shows the electron-density surfaces for these compounds, and the surface represents the values of the electron density at a resolution of 0.002 units of charge per unit of surface area. The most negative electrostatic potential is represented in red and the most positive electrostatic potential is represented in blue. The range of the electrostatic potential varies from −60 kcal mol^{-1} to +20 kcal mol^{-1}.‡ The outcome suggests that the electrostatic potential fields over the pyridazine and pyrazine rings are rather positive even compared with that of **2**-Cl_4. Generally the intervention of an aziridiniumimide has been recognized in the reactions of 4-substituted 1,2,4-triazole-3,5(4*H*)-diones,[32–36] although a recent theoretical study suggested an open biradical intermediate.[37] Thus, the ene reaction of fused pyridazines and pyrazines with PTAD would proceed by means of an aziridiniumimide-like transition state. The complete *syn* preferences for the reactions with isopropylidenenorbornadienes **3**–**5** and **9**–**12** might be attributed to the homoaromatic stabilization by electron donation from the endocyclic double bond (**68**; see Chart 2). However, even in the absence of the endocyclic double bonds, the fused pyridazines **6** and **7** as well as the pyrazines **13**–**16** exclusively preferred *syn* attack of PTAD. The results are in striking contrast to that of **2**, and the π-facial selectivity can be predominantly ascribed to the electrostatic interaction between the heteroaromatic rings and a negative charge developed in the zwitterionic polar transition state **69**. Only in the reaction of the pyridazine *N*-oxide **8** with PTAD was the formation of the *anti* isomer (**37**) observed. However, the electrostatic potential field surface over the pyridazine ring of **8** seems to be more positive than that of **6**. This result suggests that the electrostatic interaction is not the only driving force for the π-facial selectivity in the present reaction, in contrast to the conclusions drawn by Houk.[16] The formation of the *anti* isomer **37** could be also ascribed to a homoaromatic stabilization (**70**).

For the reactions of MCPBA[38,39] and NBS,[40–42] less polar transition states are presumed. Therefore, stabilization by the electrostatic interaction decreases and the formation of *anti* isomers would arise possibly due to the homoaromatic stabilization by heteroaromatic rings (**71**). However, the *anti* preference for the reactions with MCPBA and NBS is smaller than that of **2**. Furthermore, predominant *syn* attack was observed for the reactions of the fused dicyanopyrazine **15**. Therefore the electrostatic interactions would still play an important role for the π-facial selections (**72**, **73**). The positive region of electrostatic potential field over the pyrazine rings of **13**–**16** seems to increase in the order **14** < **13** < **16** < **15**, as depicted in Fig. 2. The order is in good agreement with the increasing *syn* preference for the reactions of **13**–**16** with MCPBA and NBS. The reactions of **8** and **13**–**15** with NBS produced more *anti* isomers than those with MCPBA. In the transition state of the reaction with NBS, the anionic center would exist far from the region over the heteroaromatic rings compared with that of the MCPBA epoxidation because the bromine–nitrogen bond is considered to be almost dissociated. Therefore, the electrostatic interaction between the heteroaromatic rings in the transition state of the reaction with NBS might not be effective for the formation of more *anti* isomers when compared with the reaction with MCPBA.

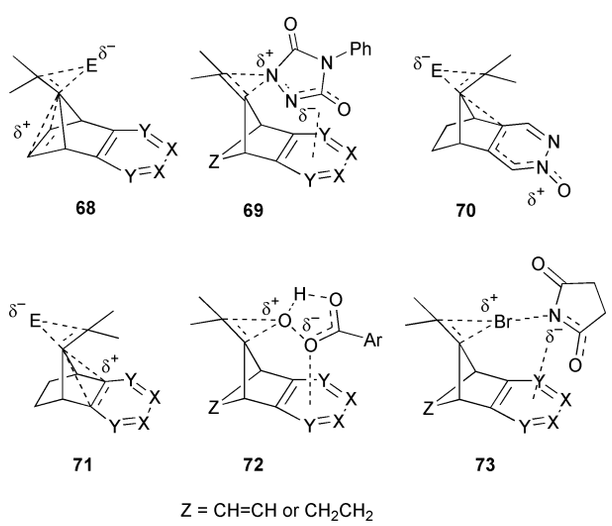


Chart 2

In conclusion, we have demonstrated that electron-deficient six-membered heteroaromatic rings such as pyridazine and pyrazine could control the π-facial selectivity of electrophilic reactions by the neighboring-group effect of six-membered heteroaromatic rings, probably due to strong electrostatic interactions able to stabilize the transition state. Predominant *syn* selectivity, which cannot be attained by the neighboring

‡ 1 cal = 4.184 J.

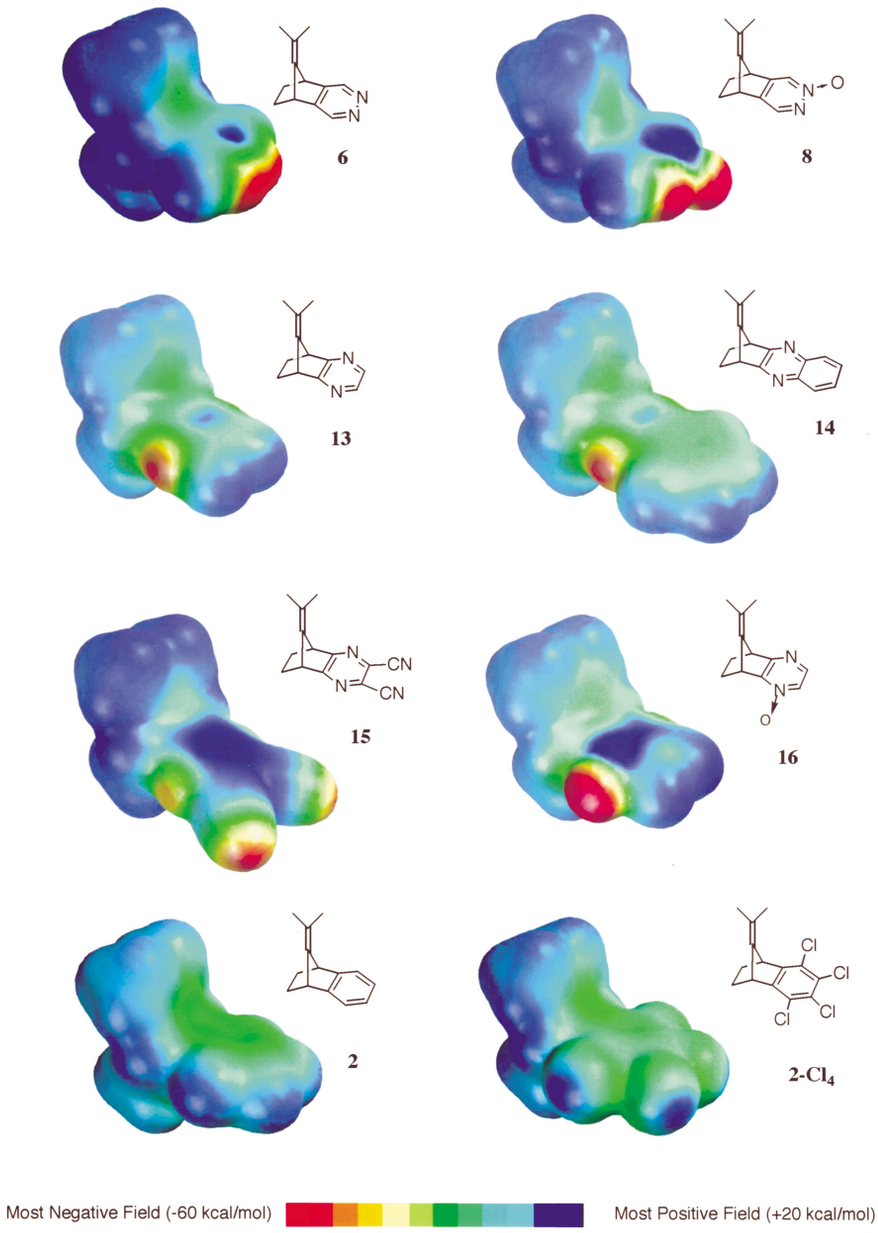


Fig. 2 Electrostatic potential surface of selected pyridazine- and pyrazine-fused isopropylidenenorbornenes calculated by PM3-MNDO method.

benzene rings, was realized by the use of six-membered heteroaromatic rings.

Experimental

General

All mps were determined with a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were obtained with a JEOL Diamond-20 spectrometer. NMR spectra were recorded with either a JEOL JNM-LA300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or JEOL JNM-LA400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometers using TMS as internal standard. *J*-values are given in Hz. Assignments of the ^{1}H and ^{13}C signals are based on DEPT, H–H COSY, and C–H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron-impact mode (70 eV). Elemental analyses were performed with a Perkin-Elmer Model 240 apparatus. Solvents were dried and purified by standard methods. Yields are based on isolated products with sufficient purity.

X-Ray diffraction data were collected at room temperature by an Enraf-Nonius CAD4 (40 kV, 26 mA) diffractometer with graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.541$ Å), ω–2θ scan technique.

Crystal data for 27. $C_{20}H_{17}N_5O_2$, $M = 359.39$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.1189(3)$, $b = 10.5252(4)$, $c = 11.2494(3)$ Å, $\alpha = 100.943(3)$, $\beta = 103.565(3)$, $\gamma = 93.725(3)°$, $V = 911.43(5)$ Å^3, $Z = 2$, $T = 293$ K, μ(Cu$K\alpha$) = 0.72 mm^{-1}, 3977 reflections measured, 3704 unique which were used in all calculations. The final R_1 was 0.0424 [$I > 2\sigma(I)$] and wR_2 (F^2) was 0.1185 (all data).§

9-(1-Methylethylidene)-5,8-dihydro-5,8-methanophthalazine 3

A solution of 4,4-diethoxybut-2-ynal[43] **17** (2.343 g, 15 mmol) and 6,6-dimethylfulvene[44] (**18**) (1.593 g, 15 mmol) in toluene (25 cm^3) was refluxed for 15 h. The solution was concentrated to give 3-(diethoxymethyl)-7-(1-methylethylidene)bicyclo[2.2.1]-hepta-2,5-diene-2-carbaldehyde **19** as a colorless oil; ν_{max}(film)/cm^{-1} 1658, 1112; δ_H(300 MHz; $CDCl_3$) 1.23 (6H, t, *J* 7, OCH_2-

§ CCDC reference number 158037. See http://www.rsc.org/suppdata/p1/b1/b101330k/ for crystallographic files in .cif or other electronic format.

CH_3), 1.47 (6H, s, Me), 3.54 (4H, m, OCH_2CH$_3$), 4.27 (1H, t, *J* 3, 1-H or 4-H), 4.56 (1H, t, *J* 3, 4-H or 1-H), 5.50 [1H, s, C*H*(OEt)$_2$], 6.87 (1H, dd, *J* 5 and 3, 5-H or 6-H), 6.92 (1H, dd, *J* 5 and 3, 6-H or 5-H), 10.17 (1H, s, CHO); δ_C(75 MHz; $CDCl_3$) 15.0 (Me), 15.1 (Me), 18.2 (Me), 18.3 (Me), 48.4 (C-1 or C-4), 53.1 (C-4 or C-1), 61.2 (CH_2), 61.4 (CH_2), 98.8 [*C*H(OEt)$_2$], 100.2 (*C*Me$_2$), 141.2 (C-5 or C-6), 142.8 (C-6 or C-5), 151.9 (C-2), 161.1 (C-7), 169.7 (C-3), 187.4 (CO); *m*/*z* 262 (M^+, 19%), 187 (M − $C_4H_{12}O$, 49), 131 (M − $C_6H_{12}O_3$, 100). Since an attempted distillation of **19** resulted in its decomposition, the crude aldehyde **19** was used for the next step without further purification.

A solution of **19** in a mixture of formic acid (85%; 3.087 g, 57 mmol) and $CHCl_3$ (90 cm^3) was refluxed for 1 h. Hydrazine hydrate (80%; 1.596 g, 26 mmol) was added and the mixture was refluxed for 0.5 h. To the mixture was added aqueous sodium hydroxide and the organic phase was separated. The aqueous phase was saturated with sodium chloride and extracted with $CHCl_3$. The combined organic phases were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica gel; AcOEt) to give **3** (1.107 g, 40%) as a light tan solid (from AcOEt); mp 204–206 °C (Found: C, 78.0; H, 6.5; N, 15.4. $C_{12}H_{12}N_2$ requires C, 78.2; H, 6.6; N, 15.2%); ν_{max}(KBr)/cm^{-1} 2913, 1544; δ_H(300 MHz; $CDCl_3$) 1.55 (6H, s, Me), 4.49 (2H, t, *J* 2, 5-H and 8-H), 6.94 (2H, t, *J* 2, 6-H and 7-H), 9.15 (2H, s, 1-H and 4-H); δ_C(75 MHz; $CDCl_3$) 18.9 (Me), 48.6 (C-5 and C-8), 106.4 (*C*Me$_2$), 142.5 (C-6 and C-7), 144.4 (C-1 and C-4), 151.6 (C-4a and C-8a), 161.1 (C-9); *m*/*z* 184 (M^+, 100%), 169 (M − Me, 49), 141 (M − C_3H_7, 44), 115 (M − $C_3H_3N_2$, 67).

2,3-Dibenzoyl-7-(1-methylethylidene)bicyclo[2.2.1]hepta-2,5-diene 21

A solution of dibenzoylacetylene[45] **20** (1.180 g, 5.1 mmol) and 6,6-dimethylfulvene **18** (588 mg, 5.3 mmol) in benzene (2 cm^3) was refluxed for 18 h. The solution was concentrated and hexane was added to the residue. The resulting solid was recrystallized from hexane to give **21** (1.390 g, 80%) as yellow plates; mp 113–115 °C (Found: C, 84.5; H, 5.9. $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9%); ν_{max}(KBr)/cm^{-1} 3050, 3012, 1654, 1643, 1596, 1278; δ_H(400 MHz; $CDCl_3$) 1.61 (6H, s, Me), 4.63 (2H, t, *J* 2, 1-H and 4-H), 7.18 (6H, m, 5-H, 6-H, and Ph), 7.35 (6H, m, Ph); δ_C(100 MHz; $CDCl_3$) 18.7 (Me), 54.8 (C-1 and C-4), 100.7 (*C*Me$_2$), 128.2, 128.4, 132.7, 137.7, 142.6 (C-5 and C-6), 158.2 [(C-2 and C-3) or C-7], 161.6 [C-7 or (C-2 and C-3)], 193.3 (CO); *m*/*z* 340 (M^+, 4%), 105 (COPh, 100), 77 (Ph, 33).

9-(1-Methylethylidene)-1,4-diphenyl-5,8-dihydro-5,8-methanophthalazine 4

A solution of **21** (1.021 g, 3.0 mmol) and hydrazine hydrate (80%; 274 mg, 4.4 mmol) in a mixture of acetic acid (15 cm^3), EtOH (40 cm^3) and water (15 cm^3) was refluxed for 3 h. Water (150 cm^3) was added, and the resulting solid was collected by vacuum filtration, and recrystallized from EtOH to give **4** (856 mg, 85%) as colorless needles; mp 224–226 °C (Found: C, 85.95; H, 6.1; N, 8.3. $C_{24}H_{20}N_2$ requires C, 85.7; H, 6.0; N, 8.3%); ν_{max}(KBr)/cm^{-1} 2913, 2854, 1444, 1238, 1137; δ_H(400 MHz; $CDCl_3$) 1.50 (6H, s, Me), 4.78 (2H, t, *J* 2, 5-H and 8-H), 7.17 (2H, t, *J* 2, 6-H and 7-H), 7.56 (6H, m, Ph), 7.90 (4H, m, Ph); δ_C(100 MHz; $CDCl_3$) 18.9 (Me), 49.5 (C-5 and C-8), 106.2 (*C*Me$_2$), 127.9, 128.3, 129.5, 136.7, 142.9 (C-6 and C-7), 149.6 (C-4a and C-8a), 152.4 (C-1 and C-4), 161.1 (C-9); *m*/*z* 336 (M^+, 98%), 321 (M − Me, 64), 293 (M − Me − N_2, 33), 202 (C_4Ph_2, 79), 106 (**18**, 100).

9-(1-Methylethylidene)-5,8-dihydro-5,8-methanophthalazine-2-oxide 5

A solution of **3** (368 mg, 2 mmol) and *m*-chloroperbenzoic acid (80%; 345 mg, 1.6 mmol) in CH_2Cl_2 (13 cm^3) was stirred at room temperature for 12 h. The solution was washed successively with aq. sodium hydrogen sulfite and aq. sodium hydrogen carbonate. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried over Na_2SO_4. After removal of the solvent, the residue was separated by column chromatography (alumina; CH_2Cl_2–AcOEt 5 : 2) to give the recovered pyridazine **3** (45 mg, 12%) and the pyridazine *N*-oxide **5** (273 mg, 78% based on consumed **3**): colorless plates (from AcOEt); mp 223 °C (decomp.) (Found: C, 71.7; H, 5.9; N, 13.8. $C_{12}H_{12}N_2O$ requires C, 72.0; H, 6.0; N, 14.0%); ν_{max}(KBr)/cm^{-1} 3029, 2910, 1610, 1444, 1373, 773, 746; δ_H(400 MHz; $CDCl_3$) 1.57 (3H, s, Me), 1.58 (3H, s, Me), 4.48 (2H, br s, 5-H and 8-H), 6.86 (1H, m, 6-H or 7-H), 6.95 (1H, m, 7-H or 6-H), 8.17 (1H, s, 1-H), 8.20 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 19.1 (Me), 19.2 (Me), 47.5 (C-5 or C-8), 48.9 (C-8 or C-5), 108.4 (*C*Me$_2$), 129.4 (C-1), 139.4 (C-4), 140.1 (C-4a), 140.8 (C-6 or C-7), 142.9 (C-7 or C-6), 158.1 (C-8a or C-9), 159.0 (C-9 or C-8a); *m*/*z* 200 (M^+, 100%), 185 (M − Me, 22), 169 (**3** − Me, 10), 143 (**3** − C_3H_5, 22), 134 (M − C_5H_6, 93), 51 (C_4H_3, 39).

9-(1-Methylethylidene)-5,6,7,8-tetrahydro-5,8-methanophthalazine 6

Under a hydrogen atmosphere, a mixture of the fused pyridazine **3** (92 mg, 0.5 mmol) and Pd/C (10%; 20 mg) in a mixture of AcOEt and EtOH (40 cm^3; 2 : 1) was stirred at room temperature for 1 h. Insoluble materials were removed by filtration and the filtrate was concentrated. Hexane was added to the residue, and the resulting solid was recrystallized from hexane–1,4-dioxane (10 : 1) to give **6** (92 mg, 99%) as colorless needles; mp 141–142 °C (Found: C, 77.1; H, 7.5; N, 15.2. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%); ν_{max}(KBr)/cm^{-1} 2947, 2871, 1581, 1542, 1444, 1371, 1281, 1155, 1101, 1003, 757, 698; δ_H(400 MHz; $CDCl_3$) 1.22 (2H, dd, *J* 12 and 5, 6-H$_{endo}$ and 7-H$_{endo}$), 1.63 (6H, s, Me), 2.03 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 3.87 (2H, m, 5-H and 8-H), 9.11 (2H, m, 1-H and 4-H); δ_C(100 MHz; $CDCl_3$) 20.0 (Me), 25.6 (C-6 and C-7), 41.3 (C-5 and C-8), 115.2 (*C*Me$_2$), 144.3 (C-1 and C-4), 146.5 [C-9 or (C-4a and C-8a)], 146.8 [(C-4a and C-8a) or C-9]; *m*/*z* 186 (M^+, 47%), 171 (M − Me, 21), 158 (M − C_2H_4, 100), 143 (M − C_3H_7, 15), 130 (M − $C_2H_4N_2$, 40), 115 (M − $C_3H_7N_2$, 30).

2,3-Dibenzoyl-7-(1-methylethylidene)bicyclo[2.2.1]hept-2-ene 22

Under a hydrogen atmosphere, a mixture of the dibenzoylnorbornadiene **21** (680 mg, 2 mmol) and Pd/C (10%; 8 mg) in AcOEt (80 cm^3) was stirred at room temperature for 2.5 h. Insoluble materials were removed by filtration and the filtrate was concentrated. Hexane was added to the residue, and the resulting solid was recrystallized from EtOH to give **22** (639 mg, 93%) as colorless rods; mp 146–147 °C (Found: C, 84.0; H, 6.4. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.5%); ν_{max}(KBr)/cm^{-1} 2964, 2933, 2910, 1643, 1591, 1577, 1448, 1335, 1273, 1236; δ_H(400 MHz; $CDCl_3$) 1.62 (2H, dd, *J* 11 and 4, 5-H$_{endo}$ and 6-H$_{endo}$), 1.69 (6H, s, Me), 1.99 (2H, m, 5-H$_{exo}$ and 6-H$_{exo}$), 3.93 (2H, br s, 1-H and 4-H), 7.18 (4H, t, *J* 8, Ph), 7.37 (6H, m, Ph); δ_C(100 MHz; $CDCl_3$) 19.8 (Me), 25.7 (C-5 and C-6), 46.7 (C-1 and C-4), 112.1 (*C*Me$_2$), 128.2, 128.5, 132.6, 138.0, 144.9 [(C-2 and C-3) or C-7], 151.1 [C-7 or (C-2 and C-3)], 193.6 (CO); *m*/*z* 342 (M^+, 15%), 314 (M − C_2H_4, 95), 237 (M − C_2H_4 − Ph, 95), 105 (COPh, 89), 77 (Ph, 100), 51 (C_4H_3, 30).

9-(1-Methylethylidene)-1,4-diphenyl-5,6,7,8-tetrahydro-5,8-methanophthalazine 7

A solution of **22** (1.030 g, 3 mmol) and hydrazine hydrate (80%; 345 mg, 5.5 mmol) in a mixture of acetic acid (10 cm^3), EtOH (40 cm^3), and water (3 cm^3) was refluxed for 1 h. Water (50 cm^3) was added and the resulting solid was collected by vacuum filtration to give **7** (856 mg, 85%) as colorless needles (from EtOH); mp 238–239 °C (Found: C, 85.35; H, 6.8; N, 8.3.

$C_{24}H_{22}N_2$ requires C, 85.2; H, 6.55; N, 8.3%); ν_{max}(KBr)/cm^{-1} 2929, 2869, 1552, 1491, 1448, 1373, 1162, 1018; δ_H(400 MHz; $CDCl_3$) 1.57 (8H, m, Me, 6-H$_{endo}$, and 7-H$_{endo}$), 2.22 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 4.12 (2H, m, 5-H and 8-H), 7.53 (6H, m, Ph), 7.94 (4H, m, Ph); δ_C(100 MHz; $CDCl_3$) 19.9 (Me), 25.7 (C-6 and C-7), 41.9 (C-5 and C-8), 114.9 (*C*Me$_2$), 128.7, 129.0, 136.8, 145.1 [(C-4a and C-8a) or C-9], 146.1 [C-9 or (C-4a and C-8a)], 152.0 (C-1 and C-4), 1C missing; *m*/*z* 338 (M$^+$, 100%), 310 (M − C_2H_4, 70), 309 (M − C_2H_5, 30), 295 (M − C_3H_7, 50), 267 (M − $C_3H_7N_2$, 15), 77 (Ph, 23).

9-(1-Methylethylidene)-5,6,7,8-tetrahydro-5,8-methanophthalazine 2-oxide 8

Under a hydrogen atmosphere, a mixture of the pyridazine *N*-oxide **5** (300 mg, 1.5 mmol) and Pd/C (10%; 13 mg) in a mixture of AcOEt and EtOH (30 cm^3; 2 : 1) was stirred at room temperature for 16 h. Insoluble materials were removed by filtration and the filtrate was concentrated. Hexane was added to the residue, and the resulting solid was recrystallized from cyclohexane to give **8** (300 mg, 99%) as colorless plates; mp 140–142 °C (Found: C, 71.3; H, 7.1; N, 13.8. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%); ν_{max}(KBr)/cm^{-1} 3099, 3026, 2947, 2927, 2871, 1610, 1448, 1385, 1279; δ_H(400 MHz; $CDCl_3$) 1.31 (2H, dd, *J* 11 and 3, 6-H$_{endo}$ and 7-H$_{endo}$), 1.64 (3H, s, Me), 1.65 (3H, s, Me), 2.04 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 3.86 (1H, d, *J* 3, 5-H or 8-H), 4.41 (1H, d, *J* 3, 8-H or 5-H), 8.12 (1H, d, 1-H), 8.21 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 20.0 (Me), 20.1 (Me), 25.8 (C-6 or C-7), 26.2 (C-7 or C-6), 40.5 (C-5 or C-8), 42.0 (C-8 or C-5), 116.4 (*C*Me$_2$), 128.0 (C-1), 137.1 (C-4a), 140.4 (C-4), 144.2 (C-9), 155.0 (C-8a); *m*/*z* 202 (M$^+$, 34%), 174 (M − C_2H_4, 100), 146 (M − C_3H_4O, 60), 131 (M − $C_2H_3N_2O$, 31), 115 (M − $C_3H_5N_2O$, 31), 77 (C_6H_5, 61).

9-(1-Methylethylidene)-5,8-dihydro-5,8-methanoquinoxaline 9

A solution of 7-(1-methylethylidene)bicyclo[2.2.1]hept-5-ene-2,3-dione[22] **23** (649 mg, 4 mmol), ethylenediamine (284 mg, 4.7 mmol), and toluene-*p*-sulfonic acid (84 mg, 0.4 mmol) in benzene (40 cm^3) was refluxed for 5 h while the produced water was removed by a Dean–Stark trap. The mixture was washed successively with aq. sodium hydrogen carbonate and brine, and dried over Na_2SO_4. Removal of the solvent afforded 9-(1-methylethylidene)-2,3,5,8-tetrahydro-5,8-methanoquinoxaline **24** as a brown oil; δ_H(300 MHz; $CDCl_3$) 1.67 (6H, s, Me), 3.37–3.61 (4H, m, 2-H and 3-H), 3.86 (2H, t, *J* 2, 5-H and 8-H), 6.49 (2H, t, *J* 2, 6-H and 7-H); δ_C(75 MHz; $CDCl_3$) 19.9 (Me), 45.9 (C-2 and C-3), 50.5 (C-5 and C-8), 118.8 (*C*Me$_2$), 137.0 (C-6 and C-7), 142.4 (C-9), 162.0 (C-4a and C-8a).

A mixture of the crude dihydropyrazine **24** and nickel peroxide[46] (4.353 g, 48 mmol) in benzene (80 cm^3) was refluxed for 3 d. Insoluble materials were removed by filtration and the filtrate was concentrated. Hexane was added to the residue and the resulting solid was recrystallized from hexane to give the pyrazine **9** (299 mg, 41%) as colorless needles; mp 128–129 °C (Found: C, 78.1; H, 6.7; N, 15.5. $C_{12}H_{12}N_2$ requires C, 78.2; H, 6.6; N, 15.2%); ν_{max}(KBr)/cm^{-1} 2976, 2937, 2908, 2850, 1583, 1348; δ_H(300 MHz; $CDCl_3$) 1.62 (6H, s, Me), 4.39 (2H, t, *J* 2, 5-H and 8-H), 6.99 (2H, t, *J* 2, 6-H and 7-H), 7.85 (2H, s, 2-H and 3-H); δ_C(75 MHz; $CDCl_3$) 19.1 (Me), 51.3 (C-5 and C-8), 109.9 (*C*Me$_2$), 137.3 (C-2 and C-3), 142.5 (C-6 and C-7), 158.1 (C-9), 166.8 (C-4a and C-8a); *m*/*z* 184 (M$^+$, 100%), 169 (M − Me, 62), 115 (M − Me − $C_2H_2N_2$, 11).

11-(1-Methylethylidene)-1,4-dihydro-1,4-methanophenazine 10

A solution of 7-(1-methylethylidene)bicyclo[2.2.1]hept-5-ene-2,3-dione **23** (162 mg, 1 mmol) and *o*-phenylenediamine (108 mg, 1 mmol) in acetic acid (2 cm^3) was refluxed for 0.5 h. Aq. sodium hydrogen carbonate was added and the product was extracted with CH_2Cl_2. The organic phase was dried over $NaSO_4$ and concentrated. Hexane was added to the residue and the resulting solid was recrystallized from hexane–AcOEt (4 : 1) to give **10** (194 mg, 83%) as colorless plates; mp 171–172 °C (Found: C, 82.3; H, 6.2; N, 12.25. $C_{16}H_{14}N_2$ requires C, 82.0; H, 6.0; N, 12.0%); ν_{max}(KBr)/cm^{-1} 3014, 2976, 2924, 2908, 1444, 1286; δ_H(300 MHz; $CDCl_3$) 1.67 (6H, s, Me), 4.48 (2H, t, *J* 2, 1-H and 4-H), 6.97 (2H, t, *J* 2, 2-H and 3-H), 7.62 (2H, m, 7-H and 8-H), 7.88 (2H, m, 6-H and 9-H); δ_C(75 MHz; $CDCl_3$) 19.4 (Me), 51.1 (C-1 and C-4), 114.2 (*C*Me$_2$), 128.4 (C-7 and C-8), 128.5 (C-6 and C-9), 139.2 (C-5a and C-9a), 141.7 (C-2 and C-3), 153.8 (C-11), 164.4 (C-4a and C-10a); *m*/*z* 234 (M$^+$, 100%), 219 (M − Me, 75).

2,3-Dicyano-9-(1-methylethylidene)-5,8-dihydro-5,8-methanoquinoxaline 11

A solution of **23** (162 mg, 1 mmol) and diaminomaleonitrile (108 mg, 1 mmol) in THF (2 cm^3) was refluxed for 4 h. The solution was concentrated and hexane was added to the residue. The resulting solid was recrystallized from hexane–AcOEt (2 : 1) to give the dicyanopyrazine **11** (226 mg, 97%) as colorless plates; mp 178–179 °C (Found: C, 71.6; H, 4.3; N, 24.15. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3; N, 23.9%); ν_{max}(KBr)/cm^{-1} 2941, 2918, 2237, 1442, 1313; δ_H(300 MHz; $CDCl_3$) 1.66 (6H, s, Me), 4.53 (2H, t, *J* 2, 5-H and 8-H), 7.03 (2H, t, *J* 2, 6-H and 7-H); δ_C(75 MHz; $CDCl_3$) 19.4 (Me), 51.2 (C-5 and C-8), 113.9 (CN), 116.7 (*C*Me$_2$), 127.5 (C-2 and C-3), 142.3 (C-6 and C-7), 155.3 (C-9), 170.1 (C-4a and C-8a); *m*/*z* 234 (M$^+$, 54%), 219 (M − Me, 100), 76 (C_6H_4, 40), 41 (C_3H_5, 44).

9-(1-Methylethylidene)-5,8-dihydro-5,8-methanoquinoxaline 1-oxide 12

A solution of the fused pyrazine **9** (230 mg, 1.3 mmol) and *m*-chloroperbenzoic acid (80%; 216 mg, 1.3 mmol) in CH_2Cl_2 (13 cm^3) was stirred at room temperature for 24 h. The organic phase was washed successively with aq. sodium hydrogen sulfite and aq. sodium carbonate, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by TLC (silica gel; hexane–AcOEt 1 : 1) to give **12** (45 mg, 28%) as colorless needles (from hexane–AcOEt 4 : 1); mp 199–200 °C (Found: C, 71.8; H, 6.2; N, 14.1. $C_{12}H_{12}N_2O$ requires C, 72.0; H, 6.0; N, 14.0%); ν_{max}(KBr)/cm^{-1} 3070, 3060, 3045, 2908, 1587, 1429, 1369; δ_H(400 MHz; $CDCl_3$) 1.61 (3H, s, Me), 1.63 (3H, s, Me), 4.48 (1H, br s, 5-H), 4.93 (1H, br s, 8-H), 7.05 (2H, br s, 6-H and 7-H), 7.63 (1H, d, *J* 5, 3-H), 7.85 (1H, d, *J* 5, 2-H); δ_C(100 MHz; $CDCl_3$) 19.2 (Me), 19.3 (Me), 45.3 (C-8), 52.1 (C-5), 110.3 (*C*Me$_2$), 130.7 (C-2 or C-3), 140.7 (C-3 or C-2), 141.2 (C-6 or C-7), 143.3 (C-7 or C-6), 151.4 (C-9), 155.8 (C-4a or C-8a), 171.9 (C-8a or C-4a); *m*/*z* 200 (M$^+$, 81%), 183 (M − O − H, 75), 168 (**9** − Me − H, 100), 131 (quinoxaline + H, 18), 115 (M − Me − $C_2H_2N_2$, 28), 51 (38).

9-(1-Methylethylidene)-5,6,7,8-tetrahydro-5,8-methanoquinoxaline 13

By a similar procedure to that described for **9**, the reaction of 7-(1-methylethylidene)bicyclo[2.2.1]heptane-2,3-dione[23] **25** (246 mg, 1.5 mmol) and ethylenediamine (103 mg, 1.7 mmol), followed by oxidation with nickel peroxide provided **13** (120 mg, 44%) by means of 9-(1-methylethylidene)-2,3,5,6,7,8-hexahydro-5,8-methanoquinoxaline **26**.

13: Colorless plates (from hexane); mp 127–128 °C (Found: C, 77.6; H, 7.6; N, 15.0. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%); ν_{max}(KBr)/cm^{-1} 2964, 2952, 2941, 2910, 1437, 1360; δ_H(400 MHz; $CDCl_3$) 1.41 (2H, dm, *J* 7, 6-H$_{endo}$ and 7-H$_{endo}$), 1.66 (6H, s, Me), 2.06 (2H, dt, *J* 7 and 2, 6-H$_{exo}$ and 7-H$_{exo}$), 3.92 (2H, t, *J* 2, 5-H and 8-H), 8.06 (2H, s, 2-H and 3-H); δ_C(100 MHz; $CDCl_3$) 20.0 (Me), 25.5 (C-6 and C-7), 45.0 (C-5 and C-8), 116.2 (*C*Me$_2$), 140.4 (C-2 and C-3), 143.9 (C-9), 162.6 (C-4a and C-8a); *m*/*z* 186 (M$^+$, 26%), 158 (M − C_2H_4, 100), 118 ($C_7H_6N_2$, 34), 65 (C_5H_5, 13).

26: A brown oil: δ_H(300 MHz; $CDCl_3$) 1.64 (2H, dm, *J* 7.5, 6-H_{endo} and 7-H_{endo}), 1.70 (6H, s, Me), 1.88 (2H, dm, *J* 7.5, 6-H_{exo} and 7-H_{exo}), 3.36 (2H, m, 2-H and 3-H), 3.46 (6H, s, 2-H and 3-H); δ_C(75 MHz; $CDCl_3$) 20.7 (Me), 26.0 (C-6 and C-7), 45.3 (C-2, C-3, C-5 and C-8), 121.7 (*C*Me_2), 134.5 (C-9), 165.4 (C-4a and C-8a).

11-(1-Methylethylidene)-1,2,3,4-tetrahydro-1,4-methanophenazine 14

By a similar procedure to that described for **10**, treatment of 7-(1-methylethylidene)bicyclo[2.2.1]heptane-2,3-dione **25** (246 mg, 1.5 mmol) and *o*-phenylenediamine (162 mg, 1.5 mmol) provided **14** (251 mg, 71%) as colorless plates (from hexane); mp 182–183 °C (Found: C, 81.35; H, 6.7; N, 11.8. $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.85%); ν_{max}(KBr)/cm^{-1} 3005, 2970, 2924, 2873, 2850, 1444, 1281; δ_H(400 MHz; $CDCl_3$) 1.59 (2H, dm, *J* 7.5, 2-H_{endo} and 3-H_{endo}), 1.71 (6H, s, Me), 2.17 (2H, dt, *J* 7.5 and 2, 2-H_{exo} and 3-H_{exo}), 4.04 (2H, t, *J* 2, 1-H and 4-H), 7.65 (2H, m, 7-H and 8-H), 7.97 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 20.2 (Me), 25.7 (C-2 and C-3), 45.3 (C-1 and C-4), 118.8 (*C*Me_2), 128.3 (C-7 and C-8), 128.7 (C-6 and C-9), 141.2 (C-5a and C-9a), 141.7 (C-11), 162.7 (C-4a and C-10a); *m*/*z* 236 (M^+, 39%), 221 (M − Me, 35), 208 (M − C_2H_4, 100), 181 (phenazine + H, 37).

2,3-Dicyano-9-(1-methylethylidene)-5,6,7,8-tetrahydro-5,8-methanoquinoxaline 15

By a similar procedure to that described for **11**, treatment of 7-(1-methylethylidene)bicyclo[2.2.1]heptane-2,3-dione **25** (164 mg, 1.0 mmol) and diaminomaleonitrile (108 mg, 1.0 mmol) provided **15** (180 mg, 76%) as colorless needles (from EtOH); mp 183–184 °C (Found: C, 71.3; H, 5.0; N, 23.9. $C_{14}H_{12}N_4$ requires C, 71.2; H, 5.1; N, 23.7%); ν_{max}(KBr)/cm^{-1} 2987, 2960, 2916, 2235, 1381; δ_H(400 MHz; DMSO-d_6) 1.39 (2H, dm, *J* 7.5, 6-H_{endo} and 7-H_{endo}), 1.66 (6H, s, Me), 2.12 (2H, dm, *J* 7.5, 6-H_{exo} and 7-H_{exo}), 4.21 (2H, s, 5-H and 8-H); δ_C(100 MHz; DMSO-d_6) 19.9 (Me), 24.4 (C-6 and C-7), 44.4 (C-5 and C-8), 114.7 (CN), 120.1 (*C*Me_2), 129.9 (C-2 and C-3), 141.3 (C-9), 165.4 (C-4a and C-8a); *m*/*z* 236 (M^+, 23%), 221 (M − Me, 39), 208 (M − C_2H_4, 100), 193 (M − C_3H_7, 65), 168 (21).

9-(1-Methylethylidene)-5,6,7,8-tetrahydro-5,8-methanoquinoxaline 1-oxide 16

Under a hydrogen atmosphere, a mixture of **12** (54 mg, 0.3 mmol) and Pd/C (10%; 30 mg) in AcOEt (20 cm^3) was stirred at room temperature for 5 d. Insoluble materials were removed by filtration and the filtrate was concentrated. Hexane was added to the residue, and the resulting solid was recrystallized from hexane–AcOEt (1 : 1) to afford **16** (53 mg, 96%) as colorless prisms; mp 181–182 °C (Found: C, 71.2; H, 6.9; N, 14.0. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%); ν_{max}(KBr)/cm^{-1} 3068, 2966, 1585, 1435, 1325; δ_H(400 MHz; $CDCl_3$) 1.46 (2H, m, 6-H_{endo} and 7-H_{endo}), 1.67 (6H, s, Me), 2.08 (2H, m, 6-H_{exo} and 7-H_{exo}), 3.96 (1H, dd, *J* 3.5 and 1.5, 5-H), 4.41 (1H, dd, *J* 3.5 and 1.5, 8-H), 7.79 (1H, d, *J* 4, 3-H), 8.02 (1H, d, *J* 4, 2-H); δ_C(100 MHz; $CDCl_3$) 19.9 (Me), 20.0 (Me), 24.7 (C-6 or C-7), 25.9 (C-7 or C-6), 39.4 (C-5), 45.5 (C-8), 117.4 (*C*Me_2), 131.9 (C-2), 141.3 (C-9), 143.1 (C-3), 147.4 (C-4a), 167.2 (C-8a); *m*/*z* 202 (M^+, 29%), 174 (M − C_2H_4, 100), 157 (M − C_2H_5O, 28), 131 (quinoxaline + H, 24), 77 (C_6H_5).

General procedure for the reaction of fused pyridazines or pyrazines with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione

A solution of a fused pyridazine or pyrazine (0.5 mmol) and 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (110 mg, 0.6 mmol) in acetonitrile (20 cm^3) was stirred at room temperature for 3 h. The solution was concentrated and acetone or ethyl acetate was added to the residue. The resulting solid was collected by vacuum filtration to give an ene-reaction product.

1-(9-Isopropenyl-5,8-dihydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 27. 95%; Colorless plates (from acetone); mp 178–179 °C (decomp.) (Found: C, 66.7; H, 5.0; N, 19.5. $C_{20}H_{17}N_5O_2$ requires C, 66.8; H, 4.8; N, 19.5%); ν_{max}(KBr)/cm^{-1} 3436, 1766, 1708, 1691, 1680; δ_H(400 MHz; DMSO-d_6; 80 °C) 1.81 (3H, s, Me), 4.70 (2H, br s, 5-H and 8-H), 5.12 (1H, br s, CH_2), 5.14 (1H, br s, CH_2), 6.79 (2H, t, *J* 2, 6-H and 7-H), 7.23 (2H, m, Ph), 7.33 (1H, m, Ph), 7.41 (2H, m, Ph), 9.23 (2H, s, 1-H and 4-H), 10.70 (1H, br, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 22.0 (Me), 53.6 (C-5 and C-8), 99.9 (C-9), 116.3 (CH_2), 125.3, 127.4, 128.3, 131.2, 139.4 (C-6 and C-7), 140.0, 145.9 (C-1 and C-4), 149.3 (C-4a and C-8a), 151.0 (CO), 151.6 (CO); *m*/*z* 359 (M^+, 29%), 183 (M − PTAD − H, 100), 130 (phthalazine, 36), 119 (PhNCO, 49), 77 (Ph, 25).

1-(9-Isopropenyl-1,4-diphenyl-5,8-dihydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 28. 99%; A white powder (from AcOEt); mp 197 °C (decomp.) (Found: C, 75.0; H, 5.0; N, 13.95. $C_{32}H_{25}N_5O_2$ requires C, 75.1; H, 4.9; N, 13.7%); ν_{max}(KBr)/cm^{-1} 3450, 1764, 1708; δ_H(400 MHz; DMSO-d_6; 80 °C) 1.80 (3H, s, Me), 5.08 (2H, br, 5-H and 8-H), 5.11 (1H, br s, CH_2), 5.17 (1H, br s, CH_2), 7.10 (2H, t, *J* 2, 6-H and 7-H), 7.16 (2H, m, NPh), 7.31 (1H, m, NPh), 7.38 (2H, m, NPh), 7.52 (2H, m, Ph), 7.58 (4H, m, Ph), 7.92 (4H, m, Ph), 10.98 (1H, br, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 21.6 (Me), 54.0 (C-5 and C-8), 98.0 (C-9), 116.2 (CH_2), 125.4, 127.4, 128.0, 128.2, 128.3, 128.6, 131.1, 136.0, 140.0 (C-6 and C-7), 140.5, 147.3 (C-4a and C-8a), 150.2 (CO), 151.4 (CO), 153.5 (C-1 and C-4); *m*/*z* 511 (M^+, 83%), 335 (M − PTAD − H, 76), 283 (diphenylphthalazine + H, 100), 119 (PhNCO, 58), 77 (Ph, 37).

1-(9-Isopropenyl-5,8-dihydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 2′-oxide 29. 95%; Colorless plates (from acetone); mp 254 °C (decomp.) (Found: C, 63.85; H, 4.6; N, 18.9. $C_{20}H_{17}N_5O_3$ requires C, 64.0; H, 4.6; N, 18.7%); ν_{max}(KBr)/cm^{-1} 3329, 1774, 1708; δ_H(400 MHz; DMSO-d_6; 80 °C) 1.79 (3H, s, Me), 4.77 (2H, br s, 5-H and 8-H), 5.12 (2H, br s, CH_2), 6.69 (1H, t, *J* 5, 6-H or 7-H), 6.76 (1H, t, *J* 5, 7-H or 6-H), 7.38 (5H, m, Ph), 8.28 (1H, s, 1-H), 8.32 (1H, s, 4-H), 10.65 (1H, br, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 22.1 (Me), 52.6 (C-5 or C-8), 53.7 (C-8 or C-5), 97.2 (C-9), 116.5 (CH_2), 125.4 (Ph), 127.4 (Ph), 128.3 (Ph), 130.9 (C-1), 131.1, 137.0, 137.2, 139.53, 139.54, 141.5 (C-4), 151.4 (CO), 152.0 (CO), 157.4 (C-8a); *m*/*z* 375 (M^+, 33%), 359 (**27**, 18), 199 (M − PTAD − H, 51), 130 (phthalazine, 34), 119 (PhNCO, 100), 77 (Ph, 31).

1-(9-Isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 34. 98%; Colorless plates (from EtOH); mp >300 °C (Found: C, 66.6; H, 5.5; N, 19.3. $C_{20}H_{19}N_5O_2$ requires C, 66.5; H, 5.3; N, 19.4%); ν_{max}(KBr)/cm^{-1} 3425, 1765, 1693; δ_H(400 MHz; DMSO-d_6; 80 °C) 1.17 (2H, dd, *J* 13 and 4, 6-H_{endo} and 7-H_{endo}), 1.87 (3H, s, Me), 2.08 (2H, m, 6-H_{exo} and 7-H_{exo}), 4.27 (2H, br s, 5-H and 8-H), 5.22 (1H, br s, CH_2), 5.24 (1H, br s, CH_2), 7.24 (2H, tm, *J* 7, Ph), 7.35 (1H, tm, *J* 7, Ph), 7.42 (2H, tm, *J* 7, Ph), 9.20 (2H, s, 1-H and 4-H), 10.61 (1H, br s, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 18.4 (Me), 22.6 (C-6 and C-7), 46.4 (C-5 and C-8), 85.8 (C-9), 116.8 (CH_2), 125.3, 127.3, 128.3, 131.2, 137.7, 144.0 (C-4a and C-8a), 145.4 (C-1 and C-4), 151.0 (CO), 151.4 (CO); *m*/*z* 361 (M^+, 24%), 185 (M − PTAD − H, 80), 158 (**6** − C_2H_4, 40), 143 (**6** − C_3H_7, 100), 119 (PhNCO, 10), 77 (Ph, 21).

1-(9-Isopropenyl-1,4-diphenyl-5,6,7,8-tetrahydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 35. 94%; A white powder (from AcOEt–1,4-dioxane 10 : 1); mp 300–301 °C (Found: C, 74.8; H, 5.55; N, 13.8. $C_{32}H_{27}N_5O_2$ requires

C, 74.8; H, 5.3; N, 13.6%); ν_{max}(KBr)/cm^{-1} 3453, 1765, 1709; δ_H(400 MHz; DMSO-d_6; 80 °C) 1.43 (2H, dd, *J* 12 and 4, 6-H$_{endo}$ and 7-H$_{endo}$), 1.86 (3H, s, Me), 2.24 (2H, br, 6-H$_{exo}$ and 7-H$_{exo}$), 4.57 (2H, br s, 5-H and 8-H), 5.24 (1H, br s, CH_2), 5.28 (1H, br s, CH_2), 7.17 (2H, dm, *J* 7, NPh), 7.31 (1H, tm, *J* 7, NPh), 7.38 (2H, tm, *J* 7, NPh), 7.52 (2H, tm, *J* 7, Ph), 7.58 (4H, tm, *J* 7, Ph), 7.96 (4H, tm, *J* 7, Ph), 10.94 (1H, br s, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 18.2 (Me), 22.7 (C-6 and C-7), 46.7 (C-5 and C-8), 84.7 (C-9), 116.7 (CH_2), 125.4, 127.3, 128.1, 128.2, 128.3, 128.6, 131.2, 136.2, 138.1, 142.0 (C-4a and C-8a), 150.1 (CO), 151.2 (CO), 153.2 (C-1 and C-4); *m*/*z* 513 (M$^+$, 19%), 337 (M − PTAD − H, 100), 119 (PhNCO, 10), 77 (Ph, 21).

A mixture of 1-(9-Isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 2′-oxides 36 (*syn*) and 37 (*anti*). 92% (**36** : **37** = 10 : 1); A light tan powder; mp >300 °C (Found: C, 63.4; H, 5.0; N, 18.6. $C_{20}H_{19}N_5O_3$ requires C, 63.65; H, 5.1; N, 18.6%).

The mixture was recrystallized from AcOEt to give **36** (143 mg, 76%) as colorless prisms: mp >300 °C (Found: C, 63.8; H, 5.0; N, 18.35%); ν_{max}(KBr)/cm^{-1} 3425, 1766, 1705, 1693; δ_H(400 MHz; DMSO-d_6, 80 °C) 1.30 (2H, dd, *J* 13 and 5, 6-H$_{endo}$ and 7-H$_{endo}$), 1.87 (3H, s, Me), 2.07 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 4.24 (2H, br s, 5-H and 8-H), 5.19 (1H, br s, CH_2), 5.24 (1H, br s, CH_2), 7.31 (3H, m, Ph), 7.41 (2H, m, Ph), 8.22 (1H, s, 1-H), 8.35 (1H, s, 4-H), 10.55 (1H, br s, NH); δ_C(100 MHz; DMSO-d_6; 80 °C) 18.7 (Me), 23.0 (C-6 or C-7), 23.5 (C-7 or C-6), 45.9 (C-5 or C-8), 47.2 (C-8 or C-5), 85.1 (C-9), 117.1 (CH_2), 125.6, 127.5, 128.4, 129.4 (C-1), 131.4, 133.9, 137.5, 142.5 (C-4), 151.5 (CO), 151.8 (CO), 153.1 (C-8a); *m*/*z* 377 (M$^+$, 3%), 201 (M − PTAD − H, 13), 173 (**8** − C_2H_5, 25), 159 (**8** − C_3H_7, 15), 119 (PhNCO, 52), 91 (**18** − Me, 100), 77 (Ph, 66).

The filtrate was concentrated and the resulting solid was collected by vacuum filtration to give a mixture of **36** and **37** (20 mg) in a ratio of 1 : 1 as a light tan powder; mp 180–190 °C.

^{1}H-NMR data for **37**: δ_H(400 MHz; DMSO-d_6; 80 °C) 1.31 (2H, dd, *J* 13 and 5, 6-H$_{endo}$ and 7-H$_{endo}$), 1.64 (3H, s, Me), 2.41 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 4.23 (2H, br s, 5-H and 8-H), 4.97 (2H, br s, CH_2), 7.29–7.48 (5H, m, Ph), 8.35 (1H, s, 1-H), 8.42 (1H, s, 4-H), 10.68 (1H, br s, NH).

1-(9-Isopropenyl-5,8-dihydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 30. 96%; Colorless needles (from acetonitrile); mp 145–146 °C (Found: C, 66.5; H, 4.65; N, 19.8. $C_{20}H_{17}N_5O_2$ requires C, 66.8; H, 4.8; N, 19.5%); ν_{max}(KBr)/cm^{-1} 3477, 1778, 1757, 1714, 1693; δ_H(400 MHz; $CDCl_3$) 1.93 (3H, s, Me), 4.75 (2H, br s, 5-H and 8-H), 5.22 (1H, s, CH_2), 5.26 (1H, s, CH_2), 6.80 (2H, t, *J* 2, 6-H and 7-H), 7.29–7.40 (5H, m, Ph), 8.15 (2H, s, 2-H and 3-H), 9.47 (1H, br s, NH); δ_C(100 MHz; $CDCl_3$) 23.3 (Me), 55.8 (C-5 and C-8), 97.9 (C-9), 117.7 (CH_2), 125.3, 128.2, 129.0, 130.9, 138.5 (C-2 and C-3), 139.6 (≻*C*=CH_2), 139.7 (C-6 and C-7), 153.2 (CO), 165.9 (C-4a and C-8a), 1C missing; *m*/*z* 359 (M$^+$, 4%), 183 (M − PTAD − H, 100), 119 (PhNCO, 77), 91 (**18** − Me, 72), 41 (C_3H_5, 37).

1-(11-Isopropenyl-1,4-dihydro-1,4-methanophenazin-11-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 31. 90%; Colorless plates (from acetonitrile); mp 243 °C (decomp.) (Found: C, 70.6; H, 4.7; N, 17.4. $C_{24}H_{19}N_5O_2$ requires C, 70.4; H, 4.7; N, 17.1%); ν_{max}(KBr)/cm^{-1} 3531, 1768, 1709; δ_H(400 MHz; $CDCl_3$) 1.98 (3H, s, Me), 4.73 (2H, br s, 1-H and 4-H), 5.26 (1H, s, CH_2), 5.35 (1H, s, CH_2), 6.76 (2H, t, *J* 2, 2-H and 3-H), 7.63 (2H, m, 7-H and 8-H), 7.89 (2H, m, 6-H and 9-H), 7.28–7.40 (5H, m, Ph), 8.28 (1H, br, NH); δ_C(100 MHz; $CDCl_3$) 23.7 (Me), 55.8 (C-1 and C-4), 95.0 (C-11), 118.3 (CH_2), 125.4, 128.3 (C-6 and C-9, or C-7 and C-8), 128.7 (C-7 and C-8, or C-6 and C-9), 129.0, 130.8, 138.9 (C-2 and C-3), 139.4 (C-5a and C-9a), 153.7 (CO), 153.8 (CO), 163.6 (C-4a and C-10a), 2C missing; *m*/*z* 409 (M$^+$, 34%), 233 (M − PTAD − H, 100), 218 (M − PTAD − CH_4, 40).

1-(2,3-Dicyano-9-isopropenyl-5,8-dihydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 32. 97%; Colorless plates (from hexane–AcOEt 1 : 1); mp 190 °C (decomp.) (Found: C, 64.3; H, 3.9; N, 24.0. $C_{22}H_{15}N_7O_2$ requires C, 64.5; H, 3.7; N, 23.95%); ν_{max}(KBr)/cm^{-1} 3514, 1776, 1711; δ_H(400 MHz; $CDCl_3$) 1.88 (3H, s, Me), 4.81 (2H, br s, 5-H and 8-H), 5.25 (1H, s, CH_2), 5.26 (1H, s, CH_2), 6.77 (2H, br s, 6-H and 7-H), 7.37–7.51 (5H, m, Ph), 8.99 (1H, br, NH); δ_C(100 MHz; $CDCl_3$) 23.3 (Me), 56.0 (C-5 and C-8), 97.5 (C-9), 113.7 (CN), 119.4 (CH_2), 125.6, 128.5 (C-2 and C-3), 128.7, 129.3, 130.5, 137.9 (≻*C*=CH_2), 139.7 (C-6 and C-7), 153.5 (CO), 153.6 (CO), 169.9 (C-4a and C-8a); *m*/*z* 409 (M$^+$, 6%), 219 (**11** − Me, 12), 181 (dicyanoquinoxaline + H, 13), 119 (PhNCO, 100), 91 (**18** − Me, 88), 41 (C_3H_5, 57).

1-(9-Isopropenyl-5,8-dihydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 1′-oxide 33. 99%; A light tan powder (from water); mp 165–166 °C (Found: C, 63.8; H, 4.8; N, 18.95. $C_{20}H_{17}N_5O_3$ requires C, 64.0; H, 4.6; N, 18.7%); ν_{max}(KBr)/cm^{-1} 3452, 1776, 1711; δ_H(400 MHz; $CDCl_3$) 1.92 (3H, s, Me), 5.21 (1H, s, 5-H), 5.23 (1H, s, 8-H), 5.30 (2H, s, CH_2), 6.87 (1H, dd, *J* 5 and 3, 6-H or 7-H), 6.96 (1H, dd, *J* 5 and 3, 7-H or 6-H), 7.29–7.41 (5H, m, Ph), 8.06 (1H, d, *J* 4, 3-H), 8.34 (1H, d, *J* 4, 2-H), 11.44 (1H, br, NH); δ_C(100 MHz; $CDCl_3$) 23.2 (Me), 51.1 (C-8), 56.9 (C-5), 97.8 (C-9), 118.2 (CH_2), 125.4, 128.1, 129.0, 131.0, 131.4 (C-2), 138.4 (C-6 or C-7), 139.6 (≻*C*=CH_2), 140.7 (C-7 or C-6), 142.9 (C-3), 150.1 (C-8a), 152.8 (CO), 153.5 (CO), 171.7 (C-4a); *m*/*z* 375 (M$^+$, 28%), 358 (M − O − H, 84), 239 (M − O − H − PhNCO, 19), 199 (M − PTAD − H, 68), 183 (**9** − H, 100), 147 (quinoxaline *N*-oxide + H, 49), 119 (PhNCO, 20), 91 (**18** − Me, 46).

1-(9-Isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 38. 96%; A white powder (from hexane–AcOEt 1 : 1); mp 131–132 °C (Found: C, 66.5; H, 5.4; N, 19.2. $C_{20}H_{19}N_5O_2$ requires C, 66.5; H, 5.3; N, 19.4%); ν_{max}(KBr)/cm^{-1} 3473, 1774, 1720, 1711; δ_H(400 MHz; $CDCl_3$) 1.44 (2H, dm, *J* 8.5, 6-H$_{endo}$ and 7-H$_{endo}$), 1.97 (3H, s, Me), 2.22 (2H, d, *J* 8.5, 6-H$_{exo}$ and 7-H$_{exo}$), 4.36 (2H, br, 5-H and 8-H), 5.26 (1H, s, CH_2), 5.30 (1H, s, CH_2), 7.28–7.40 (5H, m, Ph), 8.35 (2H, s, 2-H and 3-H), 9.57 (1H, br, NH); δ_C(100 MHz; $CDCl_3$) 19.4 (Me), 23.3 (C-6 and C-7), 49.6 (C-5 and C-8), 84.2 (C-9), 118.1 (CH_2), 125.3, 128.1, 129.0, 131.1, 137.5 (≻*C*=CH_2), 141.9 (C-2 and C-3), 152.6 (CO), 152.9 (CO), 160.7 (C-4a and C-8a); *m*/*z* 361 (M$^+$, 24%), 185 (M − PTAD − H, 100), 143 (**13** − C_3H_7, 59), 119 (PhNCO, 18), 77 (Ph, 22).

1-(11-Isopropenyl-1,2,3,4-tetrahydro-1,4-methanophenazin-11-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 39. 89%; A white powder (from bromobenzene); mp >300 °C (Found: C, 70.1; H, 5.0; N, 17.05. $C_{24}H_{21}N_5O_2$ requires C, 70.1; H, 5.1; N, 17.0%); ν_{max}(KBr)/cm^{-1} 3465, 1776, 1705; δ_H(400 MHz; DMSO-d_6) 1.43 (2H, dm, *J* 8.5, 2-H$_{endo}$ and 3-H$_{endo}$), 1.92 (3H, s, Me), 2.18 (2H, d, *J* 8.5, 2-H$_{exo}$ and 3-H$_{exo}$), 4.40 (2H, br, 1-H and 4-H), 5.29 (1H, s, CH_2), 5.36 (1H, s, CH_2), 7.22–7.42 (5H, m, Ph), 7.74 (2H, m, 7-H and 8-H), 8.02 (2H, m, 6-H and 9-H), 11.16 (1H, br s, NH); δ_C(100 MHz; DMSO-d_6) 18.9 (Me), 23.3 (C-2 and C-3), 48.9 (C-1 and C-4), 82.2 (C-11), 118.0 (CH_2), 126.0, 127.9, 128.5 (C-6 and C-9, or C-7 and C-8), 128.6 (C-7 and C-8, or C-6 and C-9), 128.8, 131.2, 137.5 (≻*C*=CH_2), 141.4 (C-5a and C-9a), 150.8 (CO), 152.5 (CO), 161.3 (C-4a and C-10a); *m*/*z* 411 (M$^+$, 22%), 235 (M − PTAD − H, 100), 193 (**14** − C_3H_7, 32), 119 (PhNCO, 18), 77 (Ph, 30), 41 (C_3H_5, 25).

1-(2,3-Dicyano-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 40. 99%; Colorless plates (from hexane–AcOEt 1 : 1); mp 290 °C

(decomp.) (Found: C, 64.0; H, 4.2; N, 23.9. $C_{22}H_{17}N_7O_2$ requires C, 64.2; H, 4.2; N, 23.8%); ν_{max}(KBr)/cm^{-1} 3436, 1770, 1702; δ_H(400 MHz; DMSO-d_6) 1.37 (2H, d, *J* 9, 6-H$_{endo}$ and 7-H$_{endo}$), 1.84 (3H, s, Me), 2.18 (2H, d, *J* 9, 6-H$_{exo}$ and 7-H$_{exo}$), 4.49 (2H, br s, 5-H and 8-H), 5.25 (1H, s, CH_2), 5.34 (1H, s, CH_2), 7.29–7.48 (5H, m, Ph), 11.03 (1H, br s, NH); δ_C(100 MHz; DMSO-d_6) 18.6 (Me), 22.1 (C-6 and C-7), 49.4 (C-5 and C-8), 83.1 (C-9), 114.7 (CN), 118.4 (CH_2), 125.9, 127.9, 128.8, 131.1, 131.2, 136.7 (>*C*=CH_2), 151.2 (CO), 152.1 (CO), 164.3 (C-4a and C-8a); *m*/*z* 411 (M$^+$, 53%), 253 (M − PTAD − H, 83), 193 (**15** − C_3H_7, 100), 119 (PhNCO, 42), 91 (**18** − Me, 35), 41 (C_3H_5, 93).

1-(9-Isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxalin-9-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione 1′-oxide 41. 97%; Colorless plates (from hexane–AcOEt 1 : 2); mp 170–171 °C (Found: C, 63.3; H, 5.4; N, 18.4. $C_{20}H_{19}N_5O_3$ requires C, 63.65; H, 5.1; N, 18.6%); ν_{max}(KBr)/cm^{-1} 3452, 1770, 1710; δ_H(400 MHz; $CDCl_3$) 1.52 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 1.96 (3H, s, Me), 2.28 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 4.73 (2H, br s, 5-H), 4.77 (1H, br s, 8-H), 5.33 (1H, s, CH_2), 5.34 (1H, s, CH_2), 7.31–7.40 (5H, m, Ph), 8.24 (1H, d, *J* 4, 3-H), 8.35 (1H, d, *J* 4, 2-H); δ_C(100 MHz; $CDCl_3$) 19.3 (Me), 22.4 (C-6 or C-7), 23.9 (C-7 or C-6), 45.2 (C-8), 50.3 (C-5), 83.7 (C-9), 118.7 (CH_2), 125.4, 128.1, 129.0, 131.1, 132.9 (C-2), 137.1 (>*C*=CH_2), 145.4 (C-3), 145.6 (C-4a), 152.8 (C=O), 153.0 (C=O), 166.1 (C-8a); *m*/*z* 377 (M$^+$, 52%), 360 (M − O − H, 24), 201 (M − PTAD − H, 39), 185 (**13** − H, 100), 143 (**13** − C_3H_7, 48), 119 (PhNCO, 37), 91 (**18** − Me, 31).

General procedure for the reaction of fused pyridazines or pyrazines with *m*-chloroperbenzoic acid

A solution of a fused pyridazine or pyrazine (0.5 mmol) and *m*-chloroperbenzoic acid (80%; 108 mg, 0.6 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 12 h. The organic phase was washed successively with aq. sodium hydrogen sulfite and aq. sodium carbonate. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried over Na_2SO_4. After removal of the solvent, *syn* and *anti* isomers were separated by TLC (silica gel) if possible.

Reaction of 5 with MCPBA. A mixture of **42** and **43**: 78% (**42** : **43** = 73 : 27); a white powder (from hexane–AcOEt 1 : 1); mp 143–146 °C (Found: C, 66.7; H, 5.6; N, 12.8. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.6; N, 13.0%); ν_{max}(KBr)/cm^{-1} 3097, 3033, 2964, 2925, 1616, 1452, 1379, 1282; δ_H(400 MHz; $CDCl_3$) 1.25 (0.8H, s, **43** Me), 1.26 (0.8H, s, **43** Me), 1.39 (2.2H, s, **42** Me), 1.40 (2.2H, s, **42** Me), 3.83 (0.73H, dm, *J* 3, **42** 5-H or 8-H), 3.85 (0.73H, dm, *J* 3, **42** 8-H or 5-H), 4.10 (0.27H, dm, *J* 3, **43** 5-H or 8-H), 4.18 (0.27H, dm, *J* 3, **43** 8-H or 5-H), 6.79 (1H, m, 6-H or 7-H), 6.88 (1H, m, 7-H or 6-H), 8.24 (1H, s, 1-H), 8.32 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 20.3 (**43** Me), 20.96 (**42** Me), 21.03 (**42** Me), 48.6 (**42** C-5 or C-8), 49.9 (**42** C-8 or C-5), 50.0 (**43** C-5 or C-8), 64.7 (**42** *C*Me$_2$), 65.2 (**43** *C*Me$_2$), 101.5 (**42** C-9), 129.7 (**43** C-1), 130.8 (**42** C-1), 135.5 (**43** C-4a), 136.7 (**43** C-6 or C-7), 136.9 (**42** C-6 or C-7), 139.0 (**42** C-7 or C-6), 139.1 (**43** C-7 or C-6), 140.9 (**42** C-4a), 141.8 (**42** C-4), 154.5 (**43** C-8a), 156.0 (**42** C-8a); CH_3, C-8 or C-5, C-9 and C-4 of **43** are missing; *m*/*z* 216 (M$^+$, 4%), 146 (M − C_4H_6O, 100), 130 (phthalazine, 28), 116 (C_9H_8, 44), 89 (42), 70 (C_4H_6O, 34).

The mixture was separated by TLC (hexane–AcOEt 1 : 2) to give **43** and a mixture of **42** and **43**.

43: A white powder (from hexane–AcOEt 1 : 1); mp 205–206 °C (Found: C, 66.8; H, 5.7; N, 13.0. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.6; N, 13.0%); ν_{max}(KBr)/cm^{-1} 3089, 3068, 3030, 2991, 2960, 1612, 1446, 1392, 1277; δ_H(300 MHz; $CDCl_3$) 1.256 (3H, s, Me), 1.263 (3H, s, Me), 3.88 (1H, dm, *J* 3, 5-H or 8-H), 3.90 (1H, dm, *J* 3, 8-H or 5-H), 6.80 (1H, m, 6-H or 7-H), 6.90 (1H, m, 7-H or 6-H), 8.24 (1H, s, 1-H), 8.32 (1H, s, 4-H); δ_C(75 MHz; $CDCl_3$) 20.3 (Me), 48.6 (C-5 or C-8), 50.0 (C-8 or C-5), 65.2 (*C*Me$_2$), 101.0 (C-9), 129.7 (C-1), 135.4 (C-4a), 136.7 (C-6 or C-7), 139.0 (C-7 or C-6), 140.9 (C-4), 154.5 (C-8a); *m*/*z* 216 (M$^+$, 1%), 146 (M − C_4H_6O, 73), 130 (phthalazine, 20), 116 (C_9H_8, 36), 89 (64), 70 (C_4H_6O, 66), 42 (100).

Reaction of 10 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 5 : 1) to give **44** (37% based on the consumed **10**), **45** (22% based on the consumed **10**), and **10** (11% recovery).

44: Colorless needles (from cyclohexane); mp 187–188 °C (Found: C, 76.85; H, 5.7; N, 11.0. $C_{16}H_{14}N_2O$ requires C, 76.8; H, 5.6; N, 11.2%); ν_{max}(KBr)/cm^{-1} 3057, 3016, 2987, 2966, 2925, 1462, 1377, 1288, 1213; δ_H(300 MHz; $CDCl_3$) 1.46 (6H, s, Me), 3.84 (2H, t, *J* 2, 1-H and 4-H), 6.88 (2H, t, *J* 2, 2-H and 3-H), 7.66 (2H, m, 7-H and 8-H), 7.97 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 21.0 (Me), 51.3 (C-1 and C-4), 63.3 (*C*Me$_2$), 97.7 (C-11), 128.8 (C-6 and C-9, or C-7 and C-8), 128.9 (C-7 and C-8, or C-6 and C-9), 138.1 (C-2 and C-3), 139.9 (C-5a and C-9a), 162.1 (C-4a and C-10a); *m*/*z* 250 (M$^+$, 15%), 180 (phenazine, 100), 70 (C_4H_6O, 42).

45: A white powder (from cyclohexane); mp 215–216 °C (Found: C, 72.3; H, 5.3; N, 10.35. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%); ν_{max}(KBr)/cm^{-1} 3060, 3018, 2989, 2958, 2929, 1577, 1510, 1340; δ_H(400 MHz; $CDCl_3$) 1.44 (3H, s, Me), 1.46 (3H, s, Me), 3.89 (1H, m, 1-H), 4.45 (1H, m, 4-H), 6.94 (2H, m, 2-H and 3-H), 7.73 (2H, m, 7-H and 8-H), 8.03 (1H, dm, *J* 8, 9-H), 8.60 (1H, dm, *J* 8, 6-H); *m*/*z* 266 (M$^+$, 1%), 196 (phenazine *N*-oxide, 100), 180 (phenazine, 25), 70 (C_4H_6O, 15).

Reaction of 11 with MCPBA. 46: 94%; Colorless needles (from hexane–AcOEt 2 : 1); mp 209–210 °C (Found: C, 67.3; H, 4.0; N, 22.6. $C_{14}H_{10}N_4O$ requires C, 67.2; H, 4.0; N, 22.4%); ν_{max}(KBr)/cm^{-1} 3003, 2976, 2939, 2237, 1458, 1321, 1296; δ_H(400 MHz; $CDCl_3$) 1.44 (6H, s, Me), 3.94 (2H, t, *J* 2, 5-H and 8-H), 6.95 (2H, t, *J* 2, 6-H and 7-H); δ_C(100 MHz; $CDCl_3$) 20.8 (Me), 51.8 (C-5 and C-8), 64.0 (*C*Me$_2$), 100.9 (C-9), 113.6 (CN), 129.0 (C-2 and C-3), 138.2 (C-6 and C-7), 167.3 (C-4a and C-8a); *m*/*z* 250 (M$^+$, 1%), 233 (M − O − H, 2), 207 (**11** − CN − H, 4), 70 (C_4H_6O, 100).

Reaction of 12 with MCPBA. 47: 94%; Colorless plates (from hexane–AcOEt 1 : 1); mp 169–170 °C (Found: C, 66.55; H, 5.7; N, 13.2. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.6; N, 13.0%); ν_{max}(KBr)/cm^{-1} 3068, 2991, 2960, 2922, 1585, 1427, 1315, 1286; δ_H(400 MHz; $CDCl_3$) 1.40 (3H, s, Me), 1.41 (3H, s, Me), 3.86 (1H, m, 5-H), 4.32 (1H, m, 8-H), 6.95 (1H, t, *J* 1.5, 6-H or 7-H), 6.96 (1H, t, *J* 1.5, 7-H or 6-H), 7.78 (1H, d, *J* 4, 3-H), 8.02 (1H, d, *J* 4, 2-H); δ_C(100 MHz; $CDCl_3$) 20.6 (Me), 20.8 (Me), 46.3 (C-5), 52.8 (C-8). 64.2 (*C*Me$_2$), 100.2 (C-9), 131.6 (C-3), 137.4 (C-2), 139.1 (C-6 or C-7), 142.4 (C-7 or C-6), 148.5 (C-4a), 168.8 (C-8a); *m*/*z* 216 (M$^+$, 0.2%), 147 (M − C_4H_5O, 10), 130 (quinoxaline, 11), 91 (**18** − Me, 10), 70 (C_4H_6O, 78), 42 (C_3H_6, 100).

Reaction of 8 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 1 : 2).

48: 40%; Colorless plates (from hexane–AcOEt 2 : 3); mp 177–178 °C (Found: C, 66.3; H, 6.5; N, 12.85. $C_{12}H_{14}N_2O_2$ requires C, 66.0; H, 6.5; N, 12.8%); ν_{max}(KBr)/cm^{-1} 3105, 2999, 2954, 1618, 1471, 1456, 1389, 1282, 1263; δ_H(400 MHz; $CDCl_3$) 1.39 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 1.41 (3H, s, Me), 1.42 (3H, s, Me), 2.18 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.13 (1H, d, *J* 3, 5-H or 8-H), 3.15 (1H, d, *J* 3, 8-H or 5-H), 8.19 (1H, s, 1-H), 8.33 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 20.5 (Me), 21.6 (Me), 23.3 (C-6 or C-7), 23.8 (C-7 or C-6), 41.2 (C-5 or C-8), 42.6 (C-8 or C-5), 62.7 (*C*Me$_2$), 88.4 (C-9), 129.5 (C-1), 135.0 (C-4a), 142.5 (C-4), 153.3 (C-8a); *m*/*z* 218 (M$^+$, 21%), 148 (M − C_4H_6O, 100), 91 (**18** − Me, 74), 65 (C_5H_5, 32).

49: 48%; Colorless needles (from hexane–AcOEt 2 : 3); mp 207–208 °C (Found: C, 66.3; H, 6.5; N, 12.85. $C_{12}H_{14}N_2O_2$ requires C, 66.0; H, 6.5; N, 12.8%); ν_{max}(KBr)/cm^{-1} 3097, 3032, 2972, 2954, 1616, 1455, 1398, 1281, 1267; δ_H(400 MHz; $CDCl_3$) 1.32 (3H, s, Me), 1.33 (3H, s, Me), 1.42 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 2.41 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.07 (1H, d, *J* 3, 5-H or 8-H), 3.10 (1H, d, *J* 3, 8-H or 5-H), 8.17 (1H, s, 1-H), 8.31 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 21.5 (Me), 24.2 (C-6 or C-7), 24.7 (C-7 or C-6), 40.6 (C-5 or C-8), 42.2 (C-8 or C-5), 63.3 (*C*Me$_2$), 85.7 (C-9), 128.7 (C-1), 133.7 (C-4a), 142.0 (C-4), 152.0 (C-8a); *m*/*z* 218 (M$^+$, 18%), 148 (M − C_4H_6O, 100), 91 (**18** − Me, 65), 65 (C_5H_5, 28).

Reaction of 13 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 1 : 1) to give the recovered pyrazine **13** (3%), **50** (36% based on the consumed **13**) and **51** (53% based on the consumed **13**), and **16** (8% based on the consumed **13**).

50: Colorless prisms (from hexane); mp 99–100 °C (Found: C, 71.55; H, 7.1; N, 13.9. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%); ν_{max}(KBr)/cm^{-1} 2976, 2951, 2923, 1379, 1367, 1105; δ_H(300 MHz; $CDCl_3$) 1.42 (6H, s, Me), 1.46 (2H, dm, *J* 7.5, 6-H$_{endo}$ and 7-H$_{endo}$), 2.19 (2H, dm, *J* 7.5, 6-H$_{exo}$ and 7-H$_{exo}$), 3.20 (2H, t, *J* 2, 5-H and 8-H), 8.23 (2H, s, 2-H and 3-H); δ_C(75 MHz; $CDCl_3$) 20.3 (Me), 23.0 (C-6 and C-7), 44.7 (C-5 and C-8), 62.0 (*C*Me$_2$), 86.9 (C-9), 141.8 (C-2 and C-3), 160.4 (C-4a and C-8a); *m*/*z* 202 (M$^+$, 29%), 159 (M − C_3H_7, 11), 131 (quinoxaline + H, 100), 77 (C_6H_5, 11).

51: Colorless prisms (from hexane); mp 115–116 °C (Found: C, 71.0; H, 7.3; N, 13.8. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.0; N, 13.85%); ν_{max}(KBr)/cm^{-1} 3012, 2962, 2943, 2868, 1365, 1122; δ_H(300 MHz; $CDCl_3$) 1.35 (6H, s, Me), 1.48 (2H, dm, *J* 7.5, 6-H$_{endo}$ and 7-H$_{endo}$), 2.41 (2H, dm, *J* 7.5, 6-H$_{exo}$ and 7-H$_{exo}$), 3.19 (2H, dd, *J* 3 and 2, 5-H and 8-H), 8.24 (2H, s, 2-H and 3-H); δ_C(75 MHz; $CDCl_3$) 21.7 (Me), 24.0 (C-6 and C-7), 44.8 (C-5 and C-8), 63.4 (*C*Me$_2$), 84.4 (C-9), 142.1 (C-2 and C-3), 159.3 (C-4a and C-8a); *m*/*z* 202 (M$^+$, 46%), 159 (M − C_3H_7, 20), 131 (quinoxaline + H, 100), 77 (C_6H_5, 15).

Reaction of 14 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 5 : 1) to give the recovered quinoxaline **14** (22%), **52** (23% based on the consumed **14**), and **53** (40% based on the consumed **14**).

52: Colorless plates (from hexane–AcOEt 2 : 1); mp 183–184 °C (Found: C, 76.1; H, 6.3; N, 11.1. $C_{16}H_{16}N_2O$ requires C, 76.2; H, 6.4; N, 11.1%); ν_{max}(KBr)/cm^{-1} 2966, 2949, 2875, 1510, 1464, 1381, 1313; δ_H(300 MHz; $CDCl_3$) 1.47 (6H, s, Me), 1.62 (2H, dm, *J* 7.5, 2-H$_{endo}$ and 3-H$_{endo}$), 2.29 (2H, dm, *J* 7.5, 2-H$_{exo}$ and 3-H$_{exo}$), 3.29 (2H, dd, *J* 2.5 and 2, 1-H and 4-H), 7.70 (2H, m, 7-H and 8-H), 8.04 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 20.5 (Me), 23.3 (C-2 and C-3), 44.9 (C-1 and C-4), 61.7 (*C*Me$_2$), 85.5 (C-11), 128.7 (C-7 and C-8), 129.0 (C-6 and C-9), 141.9 (C-5a and C-9a), 161.0 (C-4a and C-10a); *m*/*z* 252 (M$^+$, 28%), 181 (phenazine + H, 100), 76 (C_6H_4, 13).

53: A white powder (from hexane–AcOEt 4 : 1); mp 177–178 °C (Found: C, 76.35; H, 6.6; N, 11.1. $C_{24}H_{21}N_5O_2$ requires C, 76.2; H, 6.4; N, 11.1%); ν_{max}(KBr)/cm^{-1} 2954, 2877, 1508, 1464, 1381, 1317; δ_H(300 MHz; $CDCl_3$) 1.37 (6H, s, Me), 1.65 (2H, dm, *J* 7.5, 2-H$_{endo}$ and 3-H$_{endo}$), 2.53 (2H, dm, *J* 7.5, 2-H$_{exo}$ and 3-H$_{exo}$), 3.30 (2H, t, *J* 2 Hz, 1-H and 4-H), 7.72 (2H, m, 7-H and 8-H), 8.04 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 21.7 (Me), 24.3 (C-2 and C-3), 45.1 (C-1 and C-4), 63.5 (*C*Me$_2$) 83.2 (C-11), 128.9 (C-7 and C-8), 129.0 (C-6 and C-9), 142.1 (C-5a and C-9a), 159.8 (C-4a and C-10a); *m*/*z* 252 (M$^+$, 46%), 181 (phenazine + H, 100), 76 (C_6H_4, 15).

Reaction of 15 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 4 : 1) to give a mixture of **54** (64%) and **55** (14%).

54: Colorless needles (from hexane–AcOEt 1 : 1); mp 185–186 °C (Found: C, 66.8; H, 4.8; N, 22.1. $C_{14}H_{12}N_4O$ requires C, 66.65; H, 4.8; N, 22.2%); ν_{max}(KBr)/cm^{-1} 2970, 2935, 2887, 2237, 1335, 1281; δ_H(400 MHz; $CDCl_3$) 1.44 (6H, s, Me), 1.52 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 2.36 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.35 (2H, m, 5-H and 8-H); δ_C(100 MHz; $CDCl_3$) 20.3 (Me), 22.4 (C-6 and C-7), 45.1 (C-5 and C-8), 62.3 (*C*Me$_2$), 86.5 (C-9), 113.5 (CN), 131.4 (C-2 and C-3), 164.3 (C-4a and C-8a); *m*/*z* 252 (M$^+$, 8%), 181 (dicyanoquinoxaline + H, 39), 69 (C_4H_5O, 100).

55: Colorless plates (from hexane–AcOEt 1 : 1); sublimation at 195 °C (sealed tube) (Found: C, 66.7; H, 4.9; N, 22.2. $C_{14}H_{12}N_4O$ requires C, 66.65; H, 4.8; N, 22.2%); ν_{max}(KBr)/cm^{-1} 2991, 2964, 2933, 2875, 2237, 1335, 1281; δ_H(400 MHz; $CDCl_3$) 1.36 (6H, s, Me), 1.54 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 2.59 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.34 (2H, br s, 5-H and 8-H); δ_C(100 MHz; $CDCl_3$) 21.5 (Me), 23.5 (C-6 and C-7), 45.0 (C-5 and C-8), 63.8 (*C*Me$_2$), 84.0 (C-9), 113.4 (CN), 131.6 (C-2 and C-3), 163.1 (C-4a and C-8a); *m*/*z* 252 (M$^+$, 8%), 184 (66), 69 (C_4H_5O, 100).

Reaction of 16 with MCPBA. A mixture of products was separated by TLC (hexane–AcOEt 1 : 1) to give **56** (37%) and **57** (45%).

56: A white powder (from hexane–AcOEt 4 : 1); mp 145–146 °C (Found: C, 66.3; H, 6.7; N, 13.1. $C_{12}H_{14}N_2O_2$ requires C, 66.0; H, 6.5; N, 12.8%); ν_{max}(KBr)/cm^{-1} 3072, 2976, 2962, 2941, 2914, 1583, 1437, 1317, 1272; δ_H(400 MHz; $CDCl_3$) 1.41 (6H, s, Me), 1.53 (2H, m, 6-H$_{endo}$ and 7-H$_{endo}$), 2.20 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 3.23 (1H, br s, 5-H), 3.69 (1H, br s, 8-H), 7.91 (1H, d, *J* 4, 3-H), 8.16 (1H, d, *J* 4, 2-H); δ_C(100 MHz; $CDCl_3$) 20.1 (Me), 20.3 (Me), 22.3 (C-6 or C-7), 23.3 (C-7 or C-6), 39.8 (C-5), 45.4 (C-8), 62.3 (*C*Me$_2$), 85.9 (C-9), 132.7 (C-3), 144.4 (C-2), 145.5 (C-4a), 165.2 (C-8a); *m*/*z* 218 (M$^+$, 15%), 147 (quinoxaline *N*-oxide + H, 24), 131 (quinoxaline + H, 100), 104 (16), 77 (C_6H_5, 18).

57: A white powder (from hexane–AcOEt 4 : 1); mp 145–146 °C (Found: C, 66.3; H, 6.45; N, 12.9. $C_{12}H_{14}N_2O_2$ requires C, 66.0; H, 6.5; N, 12.8%); ν_{max}(KBr)/cm^{-1} 3114, 2866, 1585, 1429, 1323, 1271; δ_H(400 MHz; $CDCl_3$) 1.37 (3H, s, Me), 1.38 (3H, s, Me), 1.56 (2H, m, 6-H$_{endo}$ and 7-H$_{endo}$), 2.44 (2H, m, 6-H$_{exo}$ and 7-H$_{exo}$), 3.20 (1H, dd, *J* 3.5 and 1.5, 5-H), 3.40 (1H, dd, *J* 3.5 and 1.5, 8-H), 7.92 (1H, d, *J* 4, 3-H), 8.16 (1H, d, *J* 4, 2-H); δ_C(100 MHz; $CDCl_3$) 21.6 (Me), 21.7 (Me), 23.2 (C-6 or C-7), 24.3 (C-7 or C-6), 39.2 (C-5), 45.3 (C-8), 63.8 (*C*Me$_2$), 83.9 (C-9), 132.8 (C-3), 144.5 (C-2), 144.6 (C-4a), 163.8 (C-8a); *m*/*z* 218 (M$^+$, 26%), 147 (quinoxaline *N*-oxide + H, 24), 131 (quinoxaline + H, 100), 104 (18), 77 (C_6H_5, 15).

General procedure for the reaction of fused pyridazines and pyrazines with *N*-bromosuccinimide

A solution of a fused pyridazine or pyrazine (0.5 mmol) and *N*-bromosuccinimide (97 mg, 0.6 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 3 h. The organic phase was washed with aq. sodium hydrogen sulfite. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was separated by TLC (silica gel).

Reaction of 6 with NBS. A mixture of products was separated by TLC (hexane–AcOEt 1 : 2) to give 9-*syn*-bromo-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazine **58** (26%) and 9-*anti*-bromo-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazine **59** (34%).

58: Colorless plates (from pentane); mp 170 °C (decomp.) (Found: C, 54.3; H, 5.0; N, 10.6. $C_{12}H_{13}BrN_2$ requires C, 54.4; H, 4.9; N, 10.6%); ν_{max}(KBr)/cm^{-1} 2989, 2974, 2958, 2918, 1550, 1448; δ_H(400 MHz; $CDCl_3$) 1.18 (2H, dm, *J* 8.5, 6-H$_{endo}$ and 7-H$_{endo}$), 2.00 (3H, s, Me), 2.19 (2H, br, 6-H$_{exo}$ and 7-H$_{exo}$), 3.85 (2H, br s, 5-H and 8-H), 5.11 (1H, d, *J* 1, CH_2), 5.26 (1H, s, CH_2), 9.21 (2H, s, 1-H and 4-H); δ_C(100 MHz; $CDCl_3$) 18.4

(Me), 23.0 (C-6 and C-7), 51.3 (C-5 and C-8), 85.6 (C-9), 114.8 (CH_2), 143.0 [(C-4a and C-8a) or $\succ C{=}CH_2$], 145.7 (C-1 and C-4), 1C missing; *m*/*z* 266 (M + 2, 74%), 264 (M^+, 74), 238 (M + 2 − C_2H_4, 7), 236 (M − C_2H_4, 7), 185 (M − Br − H, 74), 143 (**6** − C_3H_7, 100), 77 (C_6H_5, 46).

59: Colorless plates (from pentane); mp 151–152 °C (Found: C, 54.7; H, 4.9; N, 10.6. $C_{12}H_{13}BrN_2$ requires C, 54.4; H, 4.9; N, 10.6%); ν_{max}(KBr)/cm^{-1} 2981, 2954, 1709, 1545, 1377; δ_H(400 MHz; $CDCl_3$) 1.33 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 1.70 (3H, d, *J* 1, Me), 2.66 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.70 (2H, t, *J* 2, 5-H and 8-H), 4.73 (1H, d, *J* 1, CH_2), 4.88 (1H, s, CH_2), 9.11 (2H, s, 1-H and 4-H); δ_C(100 MHz; $CDCl_3$) 20.8 (Me), 25.5 (C-6 and C-7), 50.1 (C-5 and C-8), 81.7 (C-9), 116.3 (CH_2), 143.0 [(C-4a and C-8a) or $\succ C{=}CH_2$], 143.4 [$\succ C{=}CH_2$ or (C-4a and C-8a)], 145.2 (C-1 and C-4); *m*/*z* 266 (M + 2, 77%), 264 (M^+, 76), 238 (M + 2 − C_2H_4, 16), 236 (M − C_2H_4, 15), 185 (M − Br − H, 100), 143 (**6** − C_3H_7, 100), 77 (C_6H_5, 57).

Reaction of 8 with NBS. A mixture of products was separated by TLC (hexane–AcOEt 1 : 2) to give 9-*syn*-bromo-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazine 2-oxide **60** (21%) and 9-*anti*-bromo-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanophthalazine 2-oxide **61** (56%).

60: Colorless prisms (from hexane–AcOEt 1 : 2), mp 142–143 °C (Found: C, 51.1; H, 4.7; N, 9.9. $C_{12}H_{13}BrN_2O$ requires C, 51.3; H, 4.7; N, 10.0%); ν_{max}(KBr)/cm^{-1} 3078, 2974, 2960, 1620, 1457, 1392; δ_H(400 MHz; $CDCl_3$) 1.29 (2H, m, 6-H$_{endo}$ and 7-H$_{endo}$), 1.99 (3H, s, Me), 2.19 (2H, br, 6-H$_{exo}$ and 7-H$_{exo}$), 3.83 (2H, br s, 5-H and 8-H), 5.12 (1H, d, *J* 1, CH_2), 5.23 (1H, s, CH_2), 8.19 (1H, s, 1-H), 8.30 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 18.4 (Me), 23.3 (C-6 or C-7), 23.6 (C-7 or C-6), 50.4 (C-5 or C-8), 51.7 (C-8 or C-5), 84.2 (C-9), 115.1 (CH_2), 129.6 (C-1), 136.6 (C-4a), 142.2 (C-4), 142.5 ($\succ C{=}CH_2$), 154.9 (C-8a); *m*/*z* 282 (M + 2, 39%), 280 (M^+, 37), 252 (14), 250 (14), 201 (M − Br − H, 86), 173 (**8** − C_2H_5, 100), 143 (**6** − C_3H_7, 39), 115 (C_9H_7, 75), 77 (C_6H_5, 57).

61: Colorless needles (from hexane–AcOEt 1 : 1), mp 154–155 °C (Found: C, 51.3; H, 4.7; N, 10.1. $C_{12}H_{13}BrN_2O$ requires C, 51.3; H, 4.7; N, 10.0%); ν_{max}(KBr)/cm^{-1} 3099, 2978, 2947, 1612, 1468, 1402; δ_H(400 MHz; $CDCl_3$) 1.43 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 1.75 (3H, d, *J* 1, Me), 2.66 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.69 (2H, br s, 5-H and 8-H), 4.82 (1H, d, *J* 1, CH_2), 4.90 (1H, s, CH_2), 8.10 (1H, s, 1-H), 8.23 (1H, s, 4-H); δ_C(100 MHz; $CDCl_3$) 20.7 (Me), 25.7 (C-6 or C-7), 26.3 (C-7 or C-6), 49.3 (C-5 or C-8), 50.7 (C-8 or C-5), 80.0 (C-9), 116.5 (CH_2), 129.0 (C-1), 133.1 (C-4a), 142.0 (C-4), 142.8 ($\succ C{=}CH_2$), 151.9 (C-8a); *m*/*z* 282 (M + 2, 44%), 280 (M^+, 44), 252 (14), 250 (14), 201 (M − Br − H, 100), 173 (**18** − C_2H_5, 48), 143 (**6** − C_3H_7, 33), 115 (C_9H_7, 56), 77 (C_6H_5, 48).

Reaction of 13 with NBS. A mixture of products was separated by TLC (hexane–AcOEt 1 : 1) to give 9-*syn*-bromo-11-isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline **62** (26%) and 9-*anti*-bromo-11-isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline **63** (50%).

62: Colorless plates (from pentane); mp 169–170 °C (Found: C, 54.25; H, 5.0; N, 10.8. $C_{12}H_{13}BrN_2$ requires C, 54.4; H, 4.9; N, 10.6%); ν_{max}(KBr)/cm^{-1} 3059, 2985, 2952, 2920, 1446, 1365; δ_H(400 MHz; $CDCl_3$) 1.36 (2H, dm, *J* 8.5, 6-H$_{endo}$ and 7-H$_{endo}$), 2.00 (3H, m, Me), 2.18 (2H, br s, 6-H$_{exo}$ and 7-H$_{exo}$), 3.87 (2H, br s, 5-H and 8-H), 5.13 (1H, m, CH_2), 5.28 (1H, s, CH_2), 8.21 (2H, s, 2-H and 3-H); δ_C(100 MHz; $CDCl_3$) 18.2 (Me), 22.9 (C-6 and C-7), 53.6 (C-5 and C-8), 83.8 (C-9), 114.7 (CH_2), 141.2 (C-2 and C-3), 142.9 ($\succ C{=}CH_2$), 162.2 (C-4a and C-8a); *m*/*z* 266 (M + 2, 20%), 264 (M^+, 20), 185 (M − Br − H, 100), 143 (**13** − C_3H_7, 42), 77 (C_6H_5, 15).

63: Colorless plates (from pentane); mp 117–118 °C (Found: C, 54.5; H, 5.1; N, 10.5. $C_{12}H_{13}BrN_2$ requires C, 54.4; H, 4.9; N, 10.6%); ν_{max}(KBr)/cm^{-1} 3047, 3008, 2951, 2916, 2877, 1444, 1363; δ_H(400 MHz; $CDCl_3$) 1.51 (2H, dm, *J* 8, 6-H$_{endo}$ and 7-H$_{endo}$), 1.78 (3H, s, Me), 2.67 (2H, dm, *J* 8, 6-H$_{exo}$ and 7-H$_{exo}$), 3.77 (2H, t, *J* 2, 5-H and 8-H), 4.78 (1H, d, *J* 1, CH_2), 4.97 (1H, s, CH_2), 8.14 (2H, s, 2-H and 3-H); δ_C(100 MHz; $CDCl_3$) 20.8 (Me), 25.4 (C-6 and C-7), 53.3 (C-5 and C-8), 79.7 (C-9), 116.5 (CH_2), 141.9 (C-2 and C-3), 143.6 ($\succ C{=}CH_2$), 159.1 (C-4a and C-8a); *m*/*z* 266 (M + 2, 16%), 264 (M^+, 22), 185 (M − Br − H, 100), 143 (**13** − C_3H_7, 39), 77 (C_6H_5, 15).

Reaction of 14 with NBS. A mixture of products was separated by TLC (hexane–AcOEt 5 : 1) to give 11-*syn*-bromo-11-isopropenyl-1,2,3,4-tetrahydro-1,4-methanophenazine **64** (22%) and 11-*anti*-bromo-11-isopropenyl-1,2,3,4-tetrahydro-1,4-methanophenazine **65** (51%).

64: Colorless needles (from hexane); mp 195–196 °C (Found: C, 60.9; H, 5.0; N, 9.1. $C_{16}H_{15}BrN_2$ requires C, 61.0; H, 4.8; N, 8.9%); ν_{max}(KBr)/cm^{-1} 3066, 2999, 2951, 2918, 2883, 1511, 1450, 1362, 1313, 1281; δ_H(400 MHz; $CDCl_3$) 1.64 (2H, dm, *J* 8.5, 2-H$_{endo}$ and 3-H$_{endo}$), 1.82 (3H, s, Me), 2.74 (2H, dm, *J* 8.5, 2-H$_{exo}$ and 3-H$_{exo}$), 3.88 (2H, t, *J* 2, 1-H and 4-H), 4.76 (1H, d, *J* 1, CH_2), 5.06 (1H, s, CH_2), 7.69 (2H, m, 7-H and 8-H), 7.99 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 18.3 (Me), 23.5 (C-2 and C-3), 53.8 (C-1 and C-4), 81.6 (C-11), 115.1 (CH_2), 128.8 (C-6 and C-9, or C-7 and C-8), 129.0 (C-7 and C-8, or C-6 and C-9), 141.4 [(C-5a and C-9a) or $\succ C{=}CH_2$], 142.5 [$\succ C{=}CH_2$ or (C-5a and C-9a)], 162.3 (C-4a and C-10a); *m*/*z* 316 (M + 2, 41%), 314 (M^+, 43), 235 (M − Br − H, 100), 207 (**14** − C_2H_5, 32), 77 (C_6H_5, 27).

65: Colorless plates (from pentane); mp 149–150 °C (Found: C, 61.1; H, 4.8; N, 8.7. $C_{16}H_{15}BrN_2$ requires C, 61.0; H, 4.8; N, 8.9%); ν_{max}(KBr)/cm^{-1} 3060, 2997, 2976, 2947, 2914, 1510, 1462, 1319, 1292; δ_H(400 MHz; $CDCl_3$) 1.64 (2H, dm, *J* 8.5, 2-H$_{endo}$ and 3-H$_{endo}$), 1.82 (3H, s, Me), 2.74 (2H, dm, *J* 8.5, 2-H$_{exo}$ and 3-H$_{exo}$), 3.88 (2H, t, *J* 2, 1-H and 4-H), 4.76 (1H, d, *J* 1, CH_2), 5.06 (1H, s, CH_2), 7.69 (2H, m, 7-H and 8-H), 7.99 (2H, m, 6-H and 9-H); δ_C(100 MHz; $CDCl_3$) 20.7 (Me), 25.9 (C-2 and C-3), 53.5 (C-1 and C-4), 78.3 (C-11), 117.3 (CH_2), 128.8 (C-6 and C-9, or C-7 and C-8), 128.9 (C-7 and C-8, or C-6 and C-9), 141.9 [(C-5a and C-9a) or $\succ C{=}CH_2$], 143.4 [$\succ C{=}CH_2$ or (C-5a and C-9a)], 159.4 (C-4a and C-10a); *m*/*z* 316 (M + 2, 46%), 314 (M^+, 47), 235 (M − Br − H, 100), 207 (**14** − C_2H_5, 41), 77 (C_6H_5, 22).

Reaction of 15 with NBS. A mixture of products was separated by TLC (hexane–AcOEt 4 : 1) to give 9-*syn*-bromo-2,3-dicyano-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline **66** (16%) and 9-*anti*-bromo-2,3-dicyano-9-isopropenyl-5,6,7,8-tetrahydro-5,8-methanoquinoxaline **67** (6%).

66: A white powder (from hexane–AcOEt 2 : 1); mp 165–166 °C (Found: C, 53.3; H, 3.7; N, 17.9. $C_{24}H_{11}BrN_4$ requires C, 53.35; H, 3.5; N, 17.8%); ν_{max}(KBr)/cm^{-1} 3093, 3010, 2974, 2956, 2925, 2239, 1452, 1371, 1338, 1282; δ_H(400 MHz; $CDCl_3$) 1.39 (2H, d, *J* 9, 6-H$_{endo}$ and 7-H$_{endo}$), 2.00 (3H, s, Me), 2.33 (2H, br m, 6-H$_{exo}$ and 7-H$_{exo}$), 4.05 (2H, s, 5-H and 8-H), 5.22 (1H, s, CH_2), 5.31 (1H, s, CH_2); δ_C(100 MHz; $CDCl_3$) 18.1 (Me), 22.6 (C-6 and C-7), 54.0 (C-5 and C-8), 80.8 (C-9), 113.5 (CN), 116.0 (CH_2), 131.0 (C-2 and C-3), 141.2 ($\succ C{=}CH_2$), 165.7 (C-4a and C-8a); *m*/*z* 316 (M + 2, 4%), 314 (M^+, 4), 235 (M − Br − H, 100), 207 (**15** − C_2H_5, 88), 193 (**15** − C_3H_7, 62), 77 (C_6H_5, 20).

67: Colorless plates (from hexane–AcOEt 1 : 1); mp 169–170 °C (Found: C, 53.5; H, 3.6; N, 17.5. $C_{24}H_{11}BrN_4$ requires C, 53.35; H, 3.5; N, 17.8%); ν_{max}(KBr)/cm^{-1} 2983, 2956, 2922, 2233, 1448, 1335; δ_H(400 MHz; $CDCl_3$) 1.54 (2H, dm, *J* 8.5, 6-H$_{endo}$ and 7-H$_{endo}$), 1.78 (3H, d, *J* 1, Me), 2.81 (2H, dm, *J* 8.5, 6-H$_{exo}$ and 7-H$_{exo}$), 3.90 (2H, t, *J* 2, 5-H and 8-H), 4.88 (1H, d, *J* 1, CH_2), 4.93 (1H, s, CH_2); δ_C(100 MHz; $CDCl_3$) 20.7 (Me), 24.9 (C-6 and C-7), 53.4 (C-5 and C-8), 113.3 (CN), 118.3 (CH_2), 131.4 (C-2 and C-3), 142.5 ($\succ C{=}CH_2$), 162.9 (C-4a and C-8a), 1C missing; *m*/*z* 316 (M + 2, 21%), 314 (M^+, 22), 235 (M − Br − H, 100), 207 (**15** − C_2H_5, 56), 193 (**15** − C_3H_7, 62), 77 (C_6H_5, 19).

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