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The Ene Reaction between Maleimides and Allyl-substituted Aromatics

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Abstract: The products from the 'ene' reaction between allyl-substituted aromatics and maleic anhydride, maleimide, *N*-phenylmaleimide and *N*-(4-phenoxyphenyl)maleimide have been isolated and characterised, and a semi-quantitative assessment of ene and enophile reactivities has been made. The reaction between *N*-phenylmaleimide and allylaromatics bearing a 1,3,5-triazine substituent has been investigated as a model for a proposed cyanate ester-*bis*-maleimide-allyl cyanate ester *ter*-polymerisation. © 1997 Elsevier Science Ltd.

INTRODUCTION

The so called 'ene reaction' belongs to the general class of pericyclic reactions and can be considered as an intermolecular signatropic [1,5]-hydrogen shift or a $[2\pi+(2\sigma,2\pi)]$ cycloaddition (Scheme 1).



The reaction was first investigated by Alder in 1943,¹ but despite several reviews² and a steady flow of new research³ it remains much less well known than many of its pericyclic relatives.⁴ The species from which the hydrogen migrates (A in Scheme 1) is called the 'ene' component, while the π -system to which it migrates (B in Scheme 1) is called the 'ene' and in addition to a concerted pericyclic mechanism,^{2.5} mechanisms involving zwitterion and diradical intermediates have been proposed;^{2b} Lewis acid catalysis is also important.⁶ The ene reaction is not limited to carbon systems and it allows a high degree of versatility in the choice of

enophile (C=C, C=C, C=N, C=O, N=N, O_2^{1} , C=S);² the range of ene components investigated to date is more limited, with the allylic system (CH-C=C) being predominant, although propargyl² and allene^{2,7} systems have been used.



Scheme 2

Our interest in the ene reaction stems from its potential for use as a polymer cross-linking process, in particular as a possible link between a cyanate ester resin (1,3,5-triazine-based) and a bismaleimide resin (Scheme 2).^{8a} Cyanate ester resins are ideally suited to many applications *e.g.* multilayer circuit boards and space applications,^{8b} but the perceived high cost has been a barrier to their widespread use.^{8c} The reaction of cyanate ester monomers with other less expensive resins is one means of reducing their cost. For example

cyanate ester/epoxy blends offer versatile handling properties, T_g values in the 160-220 °C range, low moisture absorption and low dielectric loss. The *coreaction* of alkenyl cyanate esters with bismaleimides *has* been found to yield materials combining the fine thermal properties of bismaleimide resins with the processability of the cyanate ester resins. ^{8d-f} Such an interaction has also been postulated by others as a key step in the *bis*-(maleimidophenyl)methane-*o*,*o*-diallylbisphenol A derived commercial 'Matrimid 5292' resin.⁹ However, the involvement of the ene reaction in these systems is still speculative and few if any 'ene intermediates' have been characterised. Indeed, despite the ubiquitous use of maleic anhydride as enophile, the ene reaction involving maleimides has not apparently been studied experimentally although a theoretical study has recently appeared.^{3b} While maleic anhydride and maleimides such as *N*-methylmaleimide and *N*-phenylmaleimide show almost identical Diels-Alder reactivity as dienophiles towards a standard diene such as cyclopentadiene,¹⁰ in more demanding cases (of which the ene reaction is an example) the maleimide is significantly less reactive than the anhydride.¹¹

Therefore, following on from our recent study of the Lewis acid-catalysed cyanate ester cyclotrimerisation reaction,¹² we have undertaken a scope and reactivity study of the ene reaction of allyl benzenes (1) with maleimides (3-5) along with maleic anhydride (2). In addition we have studied the reaction between the *tris*-allylphenoxytriazine (12) and *N*-phenylmaleimide (4) as a model for the proposed cyanate ester resin-*bis*-maleimide cross-linking.

RESULTS AND DISCUSSION

Allylarenes.

Heating of the allylarenes (1) with maleic anhydride (2,5-furandione) (2) or the maleimides (2,5pyrollediones) (3-5) in 1,2,4-trichlorbenzene containing quinol (as a free radical scavenger) at 180-200 °C for 24 h gave the 3-(3-arylprop-2-enyl)dihydro-2,5-furandiones (6) and the 3-(3-arylprop-2-enyl)-2,5pyrollidinediones (7-9) shown in Scheme 3.

The products were isolated by vacuum distillation in up to 30% yield and were homogenous by ¹H NMR. Purification for characterisation was by recystallisation from ethanol-water or by column chromatography (SiO₂) followed by recrystallisation. Product (6-9) identities were confirmed by the CHN microanalyses and by comparison of the ¹H NMR spectra with those of compounds 6b-9b (X = 2-CH₃) whose ¹H and ¹³C NMR signals were fully assigned (Table 1) from ¹H,¹H COSY, ¹H,¹³C COSY and ¹³C DEPT experiments as well as consideration of $\delta_{\rm H}$, $\delta_{\rm C}$ and $J_{\rm H,H}$ values.



Scheme 3

Considering compound **8b** for example, the three proton singlet at 2.33 ppm was unambiguously assigned to the methyl protons, while the double triplet at 6.19 ppm was assigned to the alkenyl H2', this being the only signal in the lowfield region coupled to aliphatic signals (1 H, 1 H COSY). The doublet at 6.83 ppm coupled to H2' was assigned to H3' (1 H, 1 H COSY) and the carbon signals at 19.9, 128.1 and 132.0 ppm were assigned to CH3, C2' and C3', respectively, from the 1 H, 1 S COSY experiment. The remaining non-methylene carbon signal (DEPT) in the aliphatic region, 40.9 ppm, was assigned to C3 and 1 H, 1 H COSY) to a discrete one proton multiplet at 3.27 ppm. The H2' alkenyl signal was coupled (1 H, 1 H COSY) to a discrete one proton multiplet at 2.82-2.90 ppm and to a one proton multiplet at 2.63-2.73 ppm, this latter multiplet partly overlapping a one-proton double-doublet centred at 2.73 ppm and another discrete one-proton double-doublet centred at 2.73 ppm and another discrete one-proton double-doublet centred at 3.05 ppm as due to the two H4 protons. The carbon signals at 34.55 and 35.3 ppm were assigned to C4 and C1', respectively, from their coupling (1 H, 1 C COSY) to the discrete H4 and H1' signals.

Ĩ	able 1. ¹³ C	and ¹ H NN	1R Chemical	l Shifts	s (ppm, relativ pyrollidi	ve to TMS inediones	5) for 3-(3- : 7b, 8b an	(2-Methylpl d 9b in Acet	henyl)prop-2-enyl :one-d ₆) dihydro-2,5-furandione 6b and 2,5-
compd	CH ₃	C	C	C4	cs	CI	C2'	C3'		Ar-C
6b	19.9	175.2	41.7 3.	4.2	171.9	34.6	127.5	132.35	126.5, 126.95, 12	8.3, 131.1, <i>136.0, 137.1</i>
Jb	19.9	180.9	42.0 3.	5.0 ^b	177.85	35.5 ^b	128.2	131.8	126.5, 127.0, 128.	.3, 131.05, <i>135.9, 137.2</i>
8 b	19.9	179.2	40.9 3.	4.55	176.2	35.3	128.1	132.0	126.5, 127.0, 127. 134.1, 135.9, 137.	.9, 128.2, 128.9, 129.6, 131.1, 3
9 b	19.9	179.3	40.9 3	14.5	176.3	35.3	128.1	132.0	119.25, 120.2, 12 129.45, 131.0, 13	4.8, 126.5,127.0, 128.2, <i>128.9,</i> 1.1, <i>135.9, 137.3, 157.7, 158.0</i>
compd	CH ₃	H3	H4 trans		$\mathrm{H4}_{cis}$	IH	((2H)	H2'	H3'	ArH
6b	2.32 (s)	3.56 (m)	$3.25 (dd, J_{4cis} = 18. J_3 = 9.6)$	6, , , , 2	96 (dd, $\frac{4}{4trans} = 18.6$, $\frac{3}{3} = 6.3$)	2.61-2 1H), 2 (m, 1F	75 (m, 80-2.90 J)	6.13 (dt, $J_{3'} = 15.6$, $J_{1'} = 7.3$)	6.82 (d, <i>J</i> ₂ ⁻ = 15.7)	7.17 (m, 3H), 7.57 (m, 1H)
7b	2.32 (s)	3.11 (m)	2.89 (dd, $J_{4cis} = 18.$ $J_3 = 9.2$)	ر بر 2 مربر 2	54 (dd, $\frac{4}{4trans} = 18.1$, $\frac{3}{3} = 4.9$)	2.50-2 1H), 2 (m, 1F	59 (m, 71-2.80 1	6.13 (dt, $J_{3'} = 15.6$, $J_{1'} = 7.2$)	6.79 (d, $J_{2'}$ = 15.7)	7.14 (m, 3H), 7.43 (m, 1H)
8 b	2.33 (s)	3.27 (m)	$3.05 (dd, J_{4cis} = 18.$ $J_3 = 9.2)$	0°	73 (dd, $\frac{4}{4trans} = 18.1$, $\frac{3}{3} = 4.8$)	2.63-2 1H), 2 (m, 1F	73 (m, 82-2.90 J)	6.19 (dt, $J_{3'} = 15.6,$ $J_{1'} = 7.1$)	6.83 (d, <i>J₂</i> = 15.7)	7.14-7.15 (m, 3H), 7.28-7.31 (m, 2H) 7.35-7.48 (m, 4H)
9b	2.33 (s)	3.27 (m)	$3.05 (dd, J_{4cis} = 18.$ $J_3 = 9.2)$,	74 (dd, $\frac{4}{4trans} = 18.0,$ 3 = 4.8)	2.63-2 1H), 2 (m, 1H	2.73 (m, 2.82-2.93 1)	6.20 (dt, $J_{3'} = 15.6$, $J_{1'} = 7.3$)	6.83 (d, $J_2^{,}$ = 15.7)	7.03-7.08 (m, 4H), 7.13-7.20 (m, 4H), 7.28-7.31 (m, 2H), 7.39-7.49 (m, 3H)

^a Signals in italics are quaternary. ^b Assignments may be interchangable.

Ene reaction between maleimides and aromatics

The higher of the two carbonyl carbon signals at 179.2 ppm was assigned to C2 since α -substitution normally raises δ_C . The H2',H3' coupling constant of *ca*. 15.6 Hz shows that the geometry about the alkene is *E*. The H4 signals both show geminal coupling of 18.0 Hz, while that at 3.05 ppm shows further coupling (to H3) of 9.2 Hz typical of a dihedral angle of *ca*. 0°, showing that this signal is due to the H4 *trans* to the arylpropenyl (cinnamyl) substituent. The further coupling, 4.8 Hz, of the other H4 signal at 2.74 ppm is consistent with it being *cis* to the arylpropenyl group. A similar analysis was used to assign the other signals shown in Table 1. All compounds **6-9** show analogous ¹H NMR spectra; in particular, all the H2',H3' coupling constants are *ca*. 15.6 Hz indicating the *E* configuration about the propenyl double bond for *all* products. Infrared assignments of v(C=O) and v(N-H) for **6b-8b** are given in Table 2.

Table 2. Infrared Data for 3-(3-(2-Methylphenyl)prop-2-enyl)dihydro-2,5-furandione **6b** and 2,5pyrollidinediones **7b**, **8b** and **9b** (Nujol Mull)

compd	v(C=O)	v(N-H)
6b	1865 (w), 1778 (s)	
7b	1765 (w), 1705 (s)	3160 (m), 1730 (s)
8b	1777 (w), 1708 (s)	
9b	1773 (w), 1703 (s)	

The anhydrides **6b** and **6d** were identified from their ¹H NMR spectra, but did not recrystallise to microanalytical purity; they were characterised as their succinic acid derivatives **6bA** and **6dA** following hydrolysis in aqueous NaOH.[#] Compound **7g** could not be recrystallised to sharp melting point and compound **6h** was an oil which was not fully characterised.

While extensive charring appeared to account for most of the low (< 30%) yield, ¹H NMR analysis of the crude reaction mixture after 24 h showed only product, starting materials and occasionally oligomerised maleimides; in particular, no evidence of Z-prop-2-enyl product was observed.¹ Heating of **1a** with maleimide **3** *in the absence of quinol*, resulted in loss of **3** over several hours to yield a precipitated solid showing a broad NMR peak at *ca*. 2.5 ppm, probably oligo-maleimide. Heating (with quinol) of the 2-bromo compound **1f** with **2** or **4** led to loss of **1f**, but no identifiable product formed, while the 2-hydroxy compound **1j** with **2**, **3** or **4** gave no identifiable product even though some **1j** remained unreacted. Apart from these, reactions leading to products which do not appear in the Experimental (*e.g.* **1h** with **3** or **5**) were not attempted.

[&]quot; The ¹H NMR and ¹³C NMR spectral data for 6b in acetone- d_6 are given in Table 1. ¹H NMR spectra for compounds 6b and 6d in CDCl₃ and for 6bA and 6dA in acetone- d_6 are given in the experimental.

¹ Except in the case of the reaction of allylbenzene (1a) with maleic anhydride (2) where a doublet at ca. 6.75 ppm, J = 10.3 Hz, (ratio of Z:E ca. 1:11) was seen in the spectrum of the crude material.

	reaction of allylbenzene 1 a at T = 187 °C after 3 h		reaction of 1-allyl-4-phenoxy benzene 1i at T = 194 °C after 3 h	
enophile	% ene 1a unreacted	% product formed	% ene 1i unreacted	% product formed
maleic anhydride 2	51	22	43	17
maleimide 3	59	11	74	11
N-phenylmaleimide 4	44	15	37	7
N-(4-phenoxyphenyl) -maleimide 5	37	13	33	9

Table 3. ¹H NMR Analysis of the Reaction of 1a and 1i with Enophiles 2, 3, 4 and 5

A semi-quantitative assessment of reactivity by ¹H NMR analysis is given in Tables 3 and 4. It is clear that there are no order of magnitude differences in reactivity between the four enophiles 2-5; the apparent low reactivity of maleimide (3) is due to its tendency to oligomerise and precipitate from solution. Likewise, the data in Table 4 show that aryl substitution has little or no effect on reactivity either with respect to electronic (compare 1e and 1g) or to steric (compare 2- and 4-substituents). Even after 3 h, it is clear that the extent of formation of product (6-9) is much less than loss of starting material (1) due to decomposition and charring as shown by darkening and increased viscosity of the solution, and by a general broadening in the aromatic region of the ¹H NMR. As after 24 h, no evidence of Z-prop-2-enyl product is observed after 3 h.

Table 4. ¹H NMR Analysis of the Reactions of Alkenes 1 with Enophile N-Phenylmaleimide at 198±2 °C

allylarene	Х	% ene 1 unreacted after 3 h	% product formed after 3 h
1a	Н	33	16
1b	2-CH ₃	39	16
lc	4-CH ₃	59	14
1 d	2-CH ₃ O	52	14
1e	4-CH ₃ O	43	12
lg	4-Br	50	10
1h *	2-PhO	44	19
li	4-PhO	37	7

^a T = 194 °C.

13480

I. D. CUNNINGHAM et al.

The lack of significant aryl substituent effect on the reaction shows that, as with aliphatic 'enes', 5,13 the mechanism involves a concerted pericyclic process, despite the allylic/benzylic nature of the migrating hydrogen with its propensity to yield carbocation, carbanion or radical intermediates. The reaction can be analysed in terms of Frontier Molecular Orbital (FMO) theory as a pericyclic intermolecular [1,5]-hydrogenshift involving a H-C-C=C (2σ , 2π) ene HOMO with a C=C (2π) enophile LUMO as shown in Scheme 4.¹⁴ There are two possible endo transition states, migration of the pro-R or the pro-S hydrogens on C1 of the allyl group, and likewise two exo transition states (Scheme 4). The observed preference for E product excludes two of the four transition states and can be rationalised in terms of a transition state with some double bond character between C1 and C2 of the allyl group. The experimental findings of Dwyer et al. have been interpreted to suggest an exo transition state for the ene reaction,¹³ but more recent ab initio modelling of the maleimide-propene transition state by Yliniemelä et al. favours an endo transition state.^{3b} This preference can be accounted for by invoking secondary interactions between 'non bond-forming' lobes of the $(2\sigma, 2\pi)$ ene system and the additional lobes of an 'extended' (6π) enophile (Scheme 4); an analogous argument accounts for the endo preference in the maleic anhydride-cyclopentadiene cycloaddition,¹⁴ although in the present case the overlap is more strained. The endo/trans-adduct transition state does appear to position the large aryl group over the enophile carbonyl region, but a degree of conjugation with the developing C1 to C2 double bond may give a more planar aryl group with minimal steric interaction; it is noteworthy that for the related maleimidebut-1-ene reaction,^{3b} AM1 calculation prefers a conformation with the ene methyl group over the enophile carbonyl.

The reason for the lack of reactivity in the case of the 2-bromo and 2-hydroxy compounds (1f and 1j) is not clear, although in the latter case it may be due to phenolic acid-catalysed resinification of the enophile since the product 8j, formed by an indirect route (see below), is stable.

Allylphenoxytriazines.

Heating of the chlorotriazinyl-substituted allylbenzene 10 with *N*-phenylmaleimide 4 under conditions as above, gave a crude material containing only charred material (aromatic peaks only) and the adduct 11. The product 11 was isolated by chromatography and identified from microanalytical data and from its characteristic ¹H NMR spectrum (compare data in experimental with typical assignments in Table 1). Reaction of the *tris*-(allylphenoxy)triazine (12) under the same conditions, (except with 3 equivalents of 4) yielded a crude reaction mixture showing extensive charring and a mixture of products (¹H NMR). Chromatography yielded small amounts (3-10% based on triazine 12) of unreacted 12, allylphenol (1j), 3-(3-(2-hydroxyphenyl)prop-2-enyl)-*N*phenyl-2,5-pyrollidinedione (8j), mono-adduct (13) and di-adduct (14) (Scheme 5). Compound 8j was identified from its microanalysis ($C_{19}H_{17}NO_3$) and from its characteristic ¹³C and ¹H NMR (see experimental and compare with Table 1). Compound 13 showed microanalysis, LRMS and HRMS data consistent with $C_{40}H_{34}N_4O_5$.



Scheme 4

Its ¹³C NMR and ¹H NMR showed peaks typical of the 3-(prop-2-enyl)-2,5-pyrollidenedione unit at 34.6 and 35.4 (C4 and C1'), 40.7 (C3), 130.1 (C2'), 2.56-2.65 and 2.78-2.86 (H1'), 2.61 (H4_{cis}) and 2.99 (H4_{trans}), 3.21 (H3), 6.37 (H2') and 6.59 (H3') ppm (compare Table 1), but also peaks typical of the allyl unit at 35.0 (C1"), 116.6 (C3"), 137.0 (C2"), 3.25 (H1"), 4.93-4.99 (H3") and 5.76-5.90 (H2"); the allyl peaks being of intensity/area *ca*. twice those of the 3-(prop-2-enyl)-2,5-pyrollidenedione peaks.¹ Compound 14, although pure by HPLC, could not be fully characterised; it was identified from its LRMS ($C_{50}H_{41}N_5O_7$) and from its ¹H and ¹³C NMR (see experimental) which were almost identical to those of 13 except that the relative allyl/propenylpyrollidenedione intensitie/areas were *ca*. 1:2 in this case. A material showing only a broad aromatic signal in its ¹H NMR and which comprised the bulk of the crude product (*ca*. 64% by weight) along with solvent (*ca*. 7% by weight) were the only other materials isolated (no symmetrical tri-adduct was detected) and no additional products were seen in the crude ¹H NMR.

A chart of the time-course of the reaction over the first 4 h is shown in Figure 1. It shows that loss of *ca*. 80% of the triazine results in only *ca*. 25% and 10% yield of mono- and di-adducts 13 and 14, respectively. Furthermore, since there is an initial 3-fold molar excess of maleimide 4, the 80% loss of 4 with only small amounts of mono- and di-adduct formed indicates extensive additional loss of maleimide, probably *via* homopolymerization.



Figure 1. Variation of Reagents and Products with Time for Reaction of *Tris*-2,4,6-(2allylphenoxy)triazine (12) with *N*-Phenylmaleimide (4) in 1,2,4-Trichlorobenzene at 201°C. Compounds from rear to front are : triazine 12, *N*-phenylmaleimide 4, mono-adduct 13 and di-adduct 14.

¹ The NMR assignments for 13 and 14 are based on DEPT and ${}^{1}H$, ${}^{1}H$ and ${}^{1}H$, ${}^{1}C$ COSY experiments (see analysis for 8b), although the C3' signal could not be unambiguously assigned. The full listings are given in the experimental section; for both compounds the two nominally unique triazine carbons appeared to give only coincident signals and one aryl or alkenyl CH carbon signal is missing amongst the others.



The phenol 1j seen in the 24 h reactions is a triazine 12 breakdown product (heating of 12 in the absence of enophile 4 yielded the phenol 1j as the only identifiable product (¹H NMR)). The phenolic 8j must also arise through breakdown of triazines 13 and 14 on prolonged (24 h) heating since direct reaction of 1j does not give an ene product with the enophiles used in this study (see above).

Despite the low yields of 'ene' products, 13 and 14, the work shows that an 'ene' reaction cross-linking of cyanate ester and bismaleimide resins *is* a viable proposition; in practice only a limited degree of cross-linking would be required rather than the quantitative results expected in organic chemistry. In a *ter*-polymerization relatively few allyl fragments would be present compared to bismaleimide (main reaction homopolymerization) and dicyanate (main reaction cyclotrimerization) and a significant level of allyl ene reaction cross-linking would be expected in the early stages of the 'main' polymerization. Further experiments confirmed that thermal cyclotrimerization of 2-allylphenyl cyanate to give the triazine 12 precedes the 'ene' reaction with the maleimide.

In the cinnamyl products in this study, the cinnamyl alkene and one of the C=C units of the 'Kekule' aromatic ring can be considered as a diene; and a *subsequent* Diels-Alder reaction between such 'dienes' and further enophile has been proposed.^{8a} However, the products would be expected to show evidence of aliphatic signals at $\delta < 2.5$ ppm in the ¹H NMR; in these experiments this region was clear, even in crude samples, and we conclude that no subsequent Diels-Alder reaction is taking place.

EXPERIMENTAL

General.

Melting points were determined using a Kofler hot stage apparatus and are uncorrected. Yields refer to chromatographically (tlc) and spectroscopically (¹H NMR) homogenous materials, unless otherwise stated. Microanalyses were carried out on a Leeman Labs Inc. CE 440 elemental analyser. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 MHz spectrometer operating at 75.47 MHz for ¹³C; the reference was TMS.

Materials.

Maleic anhydride (2), maleimide (3), N-phenylmaleimide (4), 4-phenoxyaniline, allylbenzene (1a), 4allylanisole (1e), 2-allylphenol (1j), 2-bromoiodobenzene, 2-bromotoluene, 4-bromotoluene, 1,4dibromobenzene, 4-bromodiphenyl ether, diphenyl ether, allyl bromide, quinol, 1,2,4-trichlorobenzene and cyanuric chloride were from the Aldrich Chemical Co. and were used as supplied.

13484

Allyl Compounds.

Literature methods were used for the preparations of: *N*-(4-phenoxyphenyl)maleimide (5) from 4phenoxyaniline and maleic anhydride¹⁵ and 2-allylanisole (1d) from 2-allylphenol.¹⁶ A grignard coupling reaction with allyl bromide was used to prepare:- 2- and 4-allyltoluene (1b and 1c, respectively) from 2- and 4bromotoluene, respectively;¹⁷ 4-allyl-1-bromobenzene (1g) from 1,4-dibromobenzene;¹⁸ 2-allyl-1bromobenzene (1f) from 2-bromo-1-iodobenzene;¹⁹ 4-allyl-1-phenoxybenzene (1i) from 4-bromodiphenyl ether;²⁰ and 2-allyl-1-phenoxybenzene (1b) from 2-bromodiphenyl ether.²¹ The 2-bromodiphenyl ether was prepared from diphenyl ether *via* 2-aminodiphenyl ether²² which was then converted to the bromo product after diazotisation.²³

The 2,4,6-*tris*-(2-allylphenoxy)-1,3,5-triazine (12) was prepared by TiCl₄-catalysed cyclotrimerisation of 2-allylphenyl cyanate prepared from cyanogen bromide and 2-allylphenol as described previously.¹²

<u>6-(2-Allylphenoxy)-2,4-dichloro-1,3,5-triazine</u> **10** : To a solution of cyanuric chloride (30.0 g, 162 mmol) in 200 mL of CHCl₃, was added dropwise a solution of 2-allylphenol (21.8 g, 162 mmol) and sodium hydroxide (7.2 g, 180 mmol) in 90 mL of water. After warming at 50 °C for 60 m, the cooled mixture was separated and the aqueous layer was extracted with CHCl₃ (2 x 50 mL). The organic layers were combined, dried (MgSO₄), filtered and concentrated *in vacuo* to give a crude yellow oil. Silica gel column chromatography (eluent: hexane) gave **10** (36.0 g, 78%) as an oil which crystallised to an analytically pure solid: mp 39-41 °C; ¹H NMR (CDCl₃) δ 3.31 (d, 2H, *J* = 6.3 Hz), 4.94-5.01 (m, 2H), 5.77-5.90 (m, 1H), 7.08-7.13 (m, 1H), 7.21-7.34 (m, 3H); ¹³C NMR (CDCl₃) δ 34.55, 116.9, 121.8, 127.45, 128.1, 131.2, 131.8, 135.45, 149.7, 171.4, 173.3. Anal. Calcd for C₉H₉Cl₂N₃O: C, 51.09; H, 3.22; N, 14.89. Found: C, 51.10; H, 3.13; N, 14.72.

General Ene Reaction.

The allyl aromatic (1) (50 mmol), enophile (2-5) (50 mmol) and quinol (5 mmol) were dissolved in 1,2,4trichlorobenzene (50 mmol). The reaction vessel was flushed with N_2 and the mixture was stirred and heated under N_2 at *ca*. 200 °C for 24 h. Vacuum distillation (*ca*. 0.1 Torr) yielded a preliminary fraction of solvent and unreacted starting material, followed by another of the product 6-9 in up to 30% yield. The products were purified by silica gel column chromatography and/or recrystallisation from ethanol-water.

3-(3-Phenylprop-2-enyl)dihydro-2.5-furandione **6a** : mp = 103-104 °C (mp_{lit} = 103 °C)¹ ; ¹H NMR δ (CDCl₃) 2.61-2.71 (m, 1H, H1'), 2.74-2.79 (m, 1H, H1'), 2.79 (dd, J_{4trans} = 18.9, J_3 = 6.3, H4_{cis}), 3.07 (dd, J_{4cis} = 18.8, J_3 = 9.8, H4_{trans}), 3.29 (m, H3), 6.07 (dt, $J_{3'}$ = 5.7, $J_{1'}$ = 7.3, H2'), 6.53 (d, $J_{2'}$ = 15.7, H3'), 7.23-7.36 (m, 5H, ArH). <u>3-(3-Phenylprop-2-enyl)-2.5-pyrollidinedione</u> **7a** : mp = 118-119 °C; ¹H NMR δ (CDCl₃) 2.49-2.59 (m, 1H, H1'), 2.55 (dd, J_{4trans} = 18.6, J_3 = 4.5, H4_{cis}), 2.70-2.80 (m, 1H, H1'), 2.84 (dd, J_{4cis} = 18.3, J_3 = 9.0, H4_{trans}), 3.03 (m, H3), 6.09 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.2, H2'), 6.49 (d, $J_{2'}$ = 15.6, H3'), 7.22-7.35 (m, 5H, ArH), 8.62 (br s, 1H, NH); Anal. calcd. for C₁₃H₁₃NO₂ : C, 72.54%; H, 6.09%; N, 6.51% - Found : C, 72.36%; H, 6.02%; N, 6.41%.

<u>N-Phenyl-3-(3-phenylprop-2-enyl)-2,5-pyrollidinedione</u> **8a** : mp = 118.5-119.5 °C; ¹H NMR δ (CDCl₃) 2.52-2.64 (m, 1H, H1'), 2.61 (dd, J_{4trans} = 18.0, J_3 = 4.3, H4_{cis}), 2.73-2.81 (m, 1H, H1'), 2.89 (dd, J_{4cis} = 18.3, J_3 = 9.4, H4_{trans}), 3.04 (m, H3), 6.10 (dt, $J_{3'}$ = 5.7, $J_{1'}$ = 7.1, H2'), 6.49 (d, $J_{2'}$ = 16.3, H3'), 7.00-7.40 (m, 10H, ArH); Anal. calcd. for C₁₉H₁₇NO₂ : C, 78.33%; H, 5.88%; N, 4.81% - Found : C, 78.17%; H, 5.85%; N, 4.78%.

<u>N-(-4-Phenoxyphenyl)-3-(3-phenylprop-2-enyl)-2.5-pyrollidinedioneand</u> 9a : mp = 114.5-115.5 °C; ¹H NMR δ (CDCl₃) 2.62-2.74 (m, 1H, H1'), 2.71 (dd, J_{4trans} = 18.6, J_3 = 4.8, H4_{cis}), 2.82-2.91 (m, 1H, H1'), 3.01 (dd, J_{4cis} = 18.3, J_3 = 9.3, H4_{trans}), 3.17 (m, H3), 6.18 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.2, H2'), 6.57 (d, $J_{2'}$ = 15.6, H3'), 7.06-7.41 (m, 14H, ArH); Anal. calcd. for C₂₅H₂₁NO₃ : C, 78.31%; H, 5.52%; N, 3.65% - Found : C, 78.34%; H, 5.48%; N, 3.69%.

<u>3-(3-(2-Methylphenyl)prop-2-enyl)dihydro-2,5-furandione</u> **6b** : mp = 72-74 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.69-2.74 (m, 1H, H1'), 2.77-2.85 (m, 1H, H1'), 2.81 (dd, $J_{4trans} = 18.8, J_3 = 6.2, H4_{cis}$), 3.09 (dd, $J_{4cis} = 18.8, J_3 = 9.8, H4_{trans}$), 3.32 (m, H3), 5.94 (dt, $J_{3'} = 15.6, J_{1'} = 7.3, H2'$), 6.75 (d, $J_{2'} = 15.6, H3'$), 7.13-7.21 (m, 3H, ArH), 7.36 (t, J = 4.4, ArH).

2-(3-(2-Methylphenyl)prop-2-enyl)butandioic acid **6bA** : mp = 139.5-142 °C; ¹H NMR δ (acetone- d_6) 2.32 (s, CH₃), 2.51-2.67 (m, 2H, H1'), 2.52-2.67 (m, H4_{cis}), 2.74 (dd, J_{4cis} = 16.9, J_3 = 8.8, H4_{trans}), 3.01 (m, H3), 6.12 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.3, H2'), 6.73 (d, $J_{2'}$ = 15.6, H3'), 7.11-7.17 (m, 3H, ArH), 7.42-7.45 (m, 1H, ArH), 10.70 (br s, 2H, CO₂H); Anal. calcd. for C₁₄H₁₆O₄ : C, 67.73%; H, 6.50% - found : C, 67.58%; H, 6.56%.

3-(3-(2-Methylphenyl)prop-2-enyl)-2.5-pyrollidinedione **7b** : mp = 127-128 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.54-2.64 (m, 1H, H1'), 2.58 (dd, $J_{4trans} = 18.2, J_3 = 4.7, H4_{cis}$), 2.73-2.82 (m, 1H, H1'), 2.87 (dd, $J_{4cis} = 18.4, J_3 = 9.1, H4_{trans}$), 3.07 (m, H3), 5.96 (dt, $J_{3'} = 15.6, J_{1'} = 7.3, H2'$), 6.71 (d, $J_{2'} = 15.6, H3'$), 7.09-7.18 (m, 3H, ArH), 7.36 (t, 1H, J = 3.7), 8.03 (br s, 1H, NH); Anal. calcd. for C₁₄H₁₅NO₂ : C, 73.07%; H, 6.60%; N, 6.04% - Found : C, 73.34%; H, 6.59%; N, 6.11%.

<u>3-(3-(2-Methylphenyl)prop-2-enyl)-N-phenyl-2,5-pyrollidinedione</u> **8b** : mp = 100-101 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.64-2.77 (m, 1H, H1'), 2.72 (dd, J_{4trans} = 18.3, J_3 = 4.6, H4_{cis}), 2.84-2.92 (m, 1H, H1'), 2.99 (dd, J_{4cis} = 18.3, J_3 = 9.2, H4_{trans}), 3.19 (m, H3), 6.02 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.0, H2'), 6.76 (d, $J_{2'}$ = 15.6, H3'), 7.16-7.20 (m, 3H, ArH), 7.25-7.27 (m, 3H, ArH), 7.36-7.49 (m, 3H, ArH); Anal. calcd. for C₂₀H₁₉NO₂ : C, 78.66%; H, 6.27%; N, 4.59% - Found : C, 78.26%; H, 6.15%; N, 4.56%.

<u>3-(3-(2-Methylphenyl)prop-2-enyl)-N-(4-phenoxyphenyl)-2.5-pyrollidinedioneand</u> **9b** : mp = 131-133 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.63-2.75 (m, 1H, H1'), 2.71 (dd, $J_{4trans} = 18.4, J_3 = 4.5, H4_{cis}$), 2.83-2.91 (m, 1H, H1'), 3.01 (dd, $J_{4cis} = 18.3, J_3 = 9.2, H4_{trans}$), 3.18 (m, H3), 6.01 (dt, $J_{3'} = 15.6, J_{1'} = 7.1, H2'$), 6.76 (d, $J_{2'} = 15.5, H3'$), 7.03-7.06 (m, 4H, ArH), 7.12-7.25 (m, 6H, ArH), 7.33-7.38 (m, 3H, ArH); Anal. calcd. for $C_{26}H_{23}NO_3 : C, 78.57\%$; H, 5.83%; N, 3.52% - Found : C, 78.43%; H, 5.74%; N, 3.54%.

<u>3-(3-(4-Methylphenyl)prop-2-enyl)dihydro-2.5-furandione</u> **6c** : mp = 95-96 °C; ¹H NMR δ (CDCl₃) 2.34 (s, CH₃), 2.59-2.69 (m, 1H, H1'), 2.72-2.79 (m, 1H, H1'), 2.79 (dd, $J_{4trans} = 19.1, J_3 = 6.2, H4_{cis}$), 3.06 (dd, $J_{4cis} = 18.8, J_3 = 9.8, H4_{trans}$), 3.29 (m, H3), 6.01 (dt, $J_{3'} = 15.7, J_{1'} = 7.3, H2'$), 6.49 (d, $J_{2'} = 15.7, H3'$), 7.13 (d, 2H, J = 7.9, ArH), 7.23 (d, 2H, J = 8.0, ArH); Anal. calcd. for C₁₄H₁₄O₃ : C, 73.03%; H, 6.13%; - Found : C, 72.74%; H, 6.06%.

<u>3-(3-(4-Methylphenyl)prop-2-enyl)-2,5-pyrollidinedione</u> 7c: mp = 166-167 °C; ¹H NMR δ (acetone- d_{δ}) 2.29 (s, CH₃), 2.46-2.56 (m, 1H, H1'), 2.51 (dd, J_{4trans} = 17.0, J_3 = 4.9, H4_{cis}), 2.67-2.76 (m, 1H, H1'), 2.84 (dd, J_{4cis} = 18.0, J_3 = 9.2, H4_{trans}), 3.07 (m, H3), 6.23 (dt, $J_{3'}$ = 15.8, $J_{1'}$ = 7.1, H2'), 6.53 (d, $J_{2'}$ = 15.8, H3'), 7.12 (d, 2H, J = 7.9, ArH), 7.29 (d, 2H, J = 8.0, ArH); Anal. calcd. for C₁₄H₁₅NO₂ : C, 73.34%; H, 6.59%; N, 6.11% - Found : C, 73.17%; H, 6.58%; N, 6.02%.

<u>3-(3-(4-Methylphenyl)prop-2-enyl)-N-phenyl-2,5-pyrollidinedione</u> **8c** : mp = 137-138 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.59-2.69 (m, 1H, H1'), 2.70 (dd, J_{4trans} = 19.2, J_3 = 4.4, H4_{cis}), 2.79-2.87 (m, 1H, H1'), 2.98 (dd, J_{4cis} = 18.3, J_3 = 9.1, H4_{trans}), 3.14 (m, H3), 6.09 (dt, $J_{3'}$ = 15.7, $J_{1'}$ = 7.3, H2'), 6.51 (d, $J_{2'}$ = 15.7, H3'), 7.12 (d, 2H, J = 7.8, ArH), 7.23-7.26 (m, 4H, ArH), 7.35-7.48 (m, 3H, ArH); Anal. calcd. for C₂₀H₁₉NO₂ : C, 78.66%; H, 6.27%; N, 4.59% - Found : C, 78.69%; H, 6.23%; N, 4.66%.

<u>3-(3-(4-Methylphenyl)prop-2-enyl)-N-(4-phenoxyphenyl)-2.5-pyrollidinedioneand</u> **9c** : mp = 143-144 °C; ¹H NMR δ (CDCl₃) 2.33 (s, CH₃), 2.59-2.69 (m, 1H, H1'), 2.68 (dd, J_{4trans} = 18.3, J_3 = 4.5, H4_{cis}), 2.78-2.86 (m,

1H, H1'), 2.98 (dd, $J_{4cis} = 18.3$, $J_3 = 9.2$, H4_{trans}), 3.14 (m, H3), 6.08 (dt, $J_{3'} = 15.7$, $J_{1'} = 7.3$, H2'), 6.51 (d, $J_{2'} = 15.7$, H3'), 7.03-7.06 (m, 4H, ArH), 7.10-7.13 (m, 3H, ArH), 7.16-7.25 (m, 4H, ArH), 7.32-7.38 (m, 2H, ArH); Anal. calcd. for C₂₆H₂₃NO₃ : C, 78.57%; H, 5.83%; N, 3.52% - Found : C, 78.44%; H, 5.67%; N, 3.43%.

3-(3-(2-Methoxyphenyl)prop-2-enyl)dihydro-2.5-furandione **6d** : mp = 115-118 °C; ¹H NMR δ (CDCl₃) 3.63 (s, CH₃O), 2.57-2.68 (m, 1H, H1'), 2.72-2.83 (m, 1H, H1'), 2.61 (dd, $J_{4trans} = 19.0, J_3 = 6.3, H4_{cis}$), 3.04 (dd, $J_{4cis} = 18.9, J_3 = 9.8, H4_{trans}$), 3.29 (m, H3), 6.06 (dt, $J_{3'} = 15.8, J_{1'} = 7.2, H2'$), 6.82 (d, $J_{2'} = 16.1, H3'$), 6.65-6.96 (m, 2H, ArH), 7.23 (m, 1H, ArH), 7.35 (m, 1H, ArH).

2-(3-(2-Methoxyphenyl)prop-2-enyl)butandioic acid **6dA** : mp = 120.5-122.5 °C; ¹H NMR δ (acetone- d_6) 3.84 (s, CH₃O), 2.47-2.65 (m, 2H, H1'), 2.47-2.65 (m, H4_{cis}), 2.72 (dd, $J_{4cis} = 17.0, J_3 = 8.8, H4_{trans}$), 2.97 (m, H3), 6.25 (dt, $J_{3'} = 15.9, J_{1'} = 7.3, H2'$), 6.78 (d, $J_{2'} = 15.9, H3'$), 6.89 (t, 1H, J = 7.5, ArH), 6.96 (d, 1H, J = 8.1, ArH), 7.21 (t, 1H, J = 7.8, ArH), 7.46 (d, 1H, J = 7.6, ArH), 10.7 (br s, 2H, CO₂H); Anal. calcd. for C₁₄H₁₆O₅ : C, 63.63%; H, 6.10% - found : C, 63.38%; H, 6.12%.

3-(3-(2-Methoxyphenyl)prop-2-enyl)-2,5-pyrollidinedione 7d: mp = 44-45 °C; ¹H NMR δ (CDCl₃) 3.80 (s, CH₃O), 2.44-2.52 (m, 1H, H1'), 2.53 (dd, J_{4trans} = 18.3, J_3 = 4.8, H4_{cis}), 2.68-2.72 (m, 1H, H1'), 2.76 (dd, J_{4cis} = 18.3, J_3 = 9.0, H4_{trans}), 2.98 (m, H3), 6.07 (dt, $J_{3'}$ = 15.9, $J_{1'}$ = 7.2, H2'), 6.78 (d, $J_{2'}$ = 16.0, H3'), 6.82-6.94 (m, 2H, ArH), 7.15-7.20 (m, 1H, ArH), 7.35 (d, 1H, J = 7.5), 9.29 (br s, 1H, NH); Anal. calcd. for C₁₄H₁₅NO₃ : C, 68.56%; H, 6.16%; N, 5.71% - Found : C, 68.77%; H, 6.21%; N, 5.40%.

3-(3-(2-Methoxyphenyl)prop-2-enyl)-*N*-phenyl-2.5-pyrollidinedione **8d** : mp = 96.5-97.5 °C; ¹H NMR δ (CDCl₃) 3.84 (s, CH₃O), 2.64-2.72 (m, 1H, H1'), 2.74 (dd, $J_{4trans} = 18.2, J_3 = 4.8, H4_{cis}$), 2.82-2.90 (m, 1H, H1'), 3.00 (dd, $J_{4cis} = 18.2, J_3 = 9.1, H4_{trans}$), 3.17 (m, H3), 6.17 (dt, $J_{3'} = 15.8, J_{1'} = 7.2, H2'$), 6.83-6.97 (m, 3H, ArH and H3'), 7.20-7.50 (m, 7H, ArH); Anal. calcd. for C₂₀H₁₉NO₃ : C, 74.75%; H, 5.96%; N, 4.36% - Found : C, 74.50%; H, 5.83%; N, 4.25%.

3-(3-(2-Methoxyphenyl)prop-2-enyl)-*N*-(4-phenoxyphenyl)-2,5-pyrollidinedioneand **9d** : mp = 103-104 °C; ¹H NMR δ (CDCl₃) 3.83 (s, CH₃O), 2.63-2.73 (m, 1H, H1'), 2.73 (dd, $J_{4trans} = 18.4, J_3 = 4.5, H4_{cis}$), 2.81-2.90 (m, 1H, H1'), 2.99 (dd, $J_{4cis} = 18.3, J_3 = 9.1, H4_{trans}$), 3.16 (m, H3), 6.15 (dt, $J_{3'} = 15.9, J_{1'} = 7.1, H2'$), 6.84-6.95 (m, 3H, ArH and H3'), 7.05 (d, 4H, J = 8.6, ArH), 7.12-7.33 (m, 7H, ArH); Anal. calcd. for C₂₆H₂₃NO₄ : C, 75.53%; H, 5.61%; N, 3.39% - Found : C, 75.20%; H, 5.43%; N, 3.35%.

3-(3-(4-Methoxyphenyl)prop-2-enyl)dihydro-2.5-furandione <u>6e</u>: mp = 104.5-105.5 °C; ¹H NMR δ (CDCl₃) 3.76 (s, CH₃O), 2.60-2.65 (m, 1H, H1'), 2.70-2.78 (m, 1H, H1'), 2.77 (dd, $J_{4trans} = 17.8, J_3 = 6.4, H4_{cis}$), 3.03 (dd, $J_{4cis} = 18.9, J_3 = 9.8, H4_{trans}$), 3.25 (m, H3), 5.90 (dt, $J_{3'} = 15.7, J_{1'} = 7.2, H2'$), 6.45 (d, $J_{2'} = 15.7, H3'$), 6.84-6.86 (m, 2H, ArH), 7.25-7.28 (m, 2H, ArH); Anal. calcd. for C₁₄H₁₄O₄ : C, 68.28%; H, 5.73% - Found : C, 68.04%; H, 5.69%.

3-(3-(4-Methoxyphenyl)prop-2-enyl)-2.5-pyrollidinedione 7e: mp = 121.5-122.5 °C; ¹H NMR δ (CDCl₃) 3.80 (s, CH₃O), 2.50-2.55 (m, 1H, H1'), 2.56 (dd, J_{4trans} = 18.5, J_3 = 4.9, H4_{cis}), 2.70-2.78 (m, 1H, H1'), 2.84 (dd, J_{4cis} = 18.4, J_3 = 9.1, H4_{trans}), 3.08 (m, H3), 5.90 (dt, $J_{3'}$ = 15.7, $J_{1'}$ = 7.2, H2'), 6.43 (d, $J_{2'}$ = 15.7, H3'), 6.83 (d, 2H, J = 8.7, ArH), 7.27 (d, 2H, J = 8.7), 8.46 (br s, 1H, NH); Anal. calcd. for C₁₄H₁₅NO₃ : C, 68.56%; H, 6.16%; N, 5.71% - Found : C, 68.34%; H, 6.13%; N, 5.83%.

3-(3-(4-Methoxyphenyl)prop-2-enyl)-N-phenyl-2.5-pyrollidinedione **8e** : mp = 131-132 °C; ¹H NMR δ (CDCl₃) 3.80 (s, CH₃O), 2.61-2.68 (m, 1H, H1'), 2.70 (dd, J_{4trans} = 18.3, J_3 = 4.5, H4_{cis}), 2.77-2.85 (m, 1H, H1'), 2.98 (dd, J_{4cis} = 18.3, J_3 = 9.1, H4_{trans}), 3.14 (m, H3), 6.00 (dt, $J_{3'}$ = 15.7, $J_{1'}$ = 7.4, H2'), 6.48 (d, $J_{3'}$ = 15.6, H3'), 6.85 (d, 2H, J = 8.6, ArH), 7.23-7.29 (m, 4H, ArH), 7.35-7.48 (m, 3H, ArH); Anal. calcd. for C₂₀H₁₉NO₃ : C, 74.75%; H, 5.96%; N, 4.36% - Found : C, 74.34%; H, 5.91%; N, 4.39%.

3-(3-(4-Methoxyphenyl)prop-2-enyl)-*N*-(4-phenoxyphenyl)-2.5-pyrollidinedioneand 9e : mp = 123-124 °C; ¹H NMR δ (CDCl₃) 3.80 (s, CH₃O), 2.61-2.71 (m, 1H, H1'), 2.69 (dd, $J_{4trans} = 18.0, J_3 = 4.4, H4_{cis}$), 2.77-2.83 (m, 1H, H1'), 2.98 (dd, $J_{4cis} = 18.3, J_3 = 9.1, H4_{trans}$), 3.14 (m, H3), 6.00 (dt, $J_{3'} = 15.7, J_{1'} = 7.2, H2'$), 6.48 (d, $J_{3'} = 15.7, H3'$), 6.84 (d, 2H, J = 8.5, ArH), 7.03-7.38 (m, 11H, ArH); Anal. calcd. for C₂₆H₂₃NO₄ : C, 75.53%; H, 5.61%; N, 3.39% - Found : C, 75.29%; H, 5.49%; N, 3.37%.

<u>3-(3-(4-Bromophenyl)prop-2-enyl)dihydro-2,5-furandione</u> **6g** : mp = 105-107 °C; ¹H NMR δ (CDCl₃) 2.60-2.70 (m, 1H, H1'), 2.73-2.82 (m, 1H, H1'), 2.77 (dd, $J_{4trans} = 18.8, J_3 = 6.3, H4_{cis}$), 3.09 (dd, $J_{4cis} = 18.8, J_3 = 9.8$, H4_{trans}), 3.31 (m, H3), 6.07 (dt, $J_{3'} = 15.7, J_{1'} = 7.3, H2'$), 6.47 (d, $J_{2'} = 15.8, H3'$), 7.20 (d, 2H, J = 8.4, ArH), 7.44 (d, 2H, J = 8.4, ArH); Anal. calcd. for C₁₃H₁₁O₃Br: C, 52.91%; H, 3.76% - Found : C, 52.89%; H, 3.72%.

<u>3-(3-(4-Bromophenyl)prop-2-enyl)-2.5-pyrollidinedione</u> 7g: A solid homogenous by ¹H NMR and which melted over a range of 165 to *ca.* 175 °C; ¹H NMR δ (CDCl₃) 2.50-2.60 (m, 1H, H1'), 2.50-2.60 (m, H4_{*cis*}), 2.71-2.78 (m, 1H, H1'), 2.87 (dd, $J_{4cis} = 18.3, J_3 = 9.1, H4_{trans}$), 3.05 (m, H3), 6.10 (dt, $J_{3'} = 15.8, J_{1'} = 7.3, H2'$), 6.44 (d, $J_{2'} = 15.7, H3'$), 7.19 (d, 2H, J = 7.5, ArH), 7.43 (d, 2H, J = 7.5), 8.01 (br s, 1H, NH).

<u>3-(3-(4-Bromophenyl)prop-2-enyl)-N-phenyl-2,5-pyrollidinedione</u> **8g** : mp = 124-125 °C; ¹H NMR δ (CDCl₃) 2.60-2.72 (m, 1H, H1'), 2.60-2.77 (m, H4_{*cis*}), 2.80-2.89 (m, 1H, H1'), 3.02 (dd, J_{4cis} = 18.3, J_3 = 9.2, H4_{*trans*}), 3.17 (m, H3), 6.16 (dt, $J_{3'}$ = 15.8, $J_{1'}$ = 7.4, H2'), 6.49 (d, $J_{3'}$ = 15.8, H3'), 7.20-7.23 (m, 4H, ArH), 7.37-7.49 (m, 5H, ArH); Anal. calcd. for C₁₉H₁₆NO₂Br: C, 61.64%; H, 4.36%; N, 3.78% - Found : C, 61.62%; H, 4.25%; N, 3.70%.

3-(3-(2-Phenoxyphenyl)prop-2-enyl)dihydro-2.5-furandione **6h** : An oil which was homogenous by ¹H NMR, but was not fully characterised; ¹H NMR δ (CDCl₃) 2.47-2.56 (m, 1H, H1'), 2.63-2.72 (m, 1H, H1'), 2.51 (dd, $J_{4trans} = 18.9, J_3 = ??, H4_{cis}$), 2.82 (dd, $J_{4cis} = 18.8, J_3 = 9.8, H4_{trans}$), 3.14 (m, H3), 6.09 (dt, $J_{3'} = 15.9, J_{1'} = 7.2, H2'$), 6.71 (d, $J_{2'} = 15.9, H3'$), 6.84-6.94 (m, 3H), 7.02-7.12 (m, 2H), 7.17-7.32 (m, 3H), 7.48 (dd, 1H, J = 7.6 and 1.5, ArH).

3-(3-(2-Phenoxyphenyl)prop-2-enyl)-*N*-phenyl-2.5-pyrollidinedione **8h** : An oil; ¹H NMR δ (CDCl₃) 2.43-2.59 (m, 1H, H1'), 2.43-2.59 (m, H4_{cis}), 2.71-2.86 (m, 1H, H1'), 2.81 (dd, $J_{4cis} = 18.6, J_3 = 9.3, H4_{trans}$), 3.01 (m, H3), 6.17 (dt, $J_{3'} = 15.9, J_{1'} = 7.2, H2'$), 6.75 (d, $J_{3'} = 15.9, H3'$), 6.64-6.92 (m, 3H, ArH), 6.99-7.49 (m, 11H, ArH); Anal. calcd. for C₂₅H₂₁NO₃ : C, 78.31%; H, 5.52%; N, 3.65% - Found : C, 78.10%; H, 5.37%; N, 3.81%.

3-(3-(4-Phenoxyphenyl)prop-2-enyl)dihydro-2,5-furandione **6i** : mp 97-98 °C; ¹H NMR δ (CDCl₃) 2.61-2.84 (m, 2H, H1'), 2.79 (dd, $J_{4trans} = 18.9, J_3 = 6.1, H4_{cis}$), 3.07 (dd, $J_{4cis} = 18.8, J_3 = 9.8, H4_{trans}$), 3.29 (m, H3), 5.98 (dt, $J_{3'} = 15.7, J_{1'} = 7.3, H2'$), 6.50 (d, $J_{2'} = 15.7, H3'$), 6.94-7.02 (m, 4H), 7.11 (t, 1H, J = 7.3, ArH), 7.26-7.39 (m, 4H); Anal. calcd. for C₁₉H₁₆O₄ : C, 74.01%; H, 5.23% - Found : C, 73.89%; H, 5.08 %.

3-(3-(4-Phenoxyphenyl)prop-2-enyl)-2,5-pyrollidinedione 7i: mp = 118-119 °C; ¹H NMR δ (CDCl₃) 2.51-2.60 (m, 1H, H1'), 2.56 (dd, J_{4trans} = 18.6, J_3 = 4.5, H4_{cis}), 2.69-2.78 (m, 1H, H1'), 2.86 (dd, J_{4cis} = 18.4, J_3 = 9.1, H4_{trans}), 3.05 (m, H3), 6.00 (dt, $J_{3'}$ = 15.7, $J_{1'}$ = 7.3, H2'), 6.47 (d, $J_{2'}$ = 15.8, H3'), 6.93-7.02 (m, 4H, ArH), 7.10 (t, 1H, J = 7.3, ArH), 7.26-7.36 (m, 9H), 8.16 (br s, NH); Anal. calcd. for C₁₉H₁₇NO₃ : C, 74.25%; H, 5.58%; N, 4.56% - Found : C, 73.53%; H, 5.51%; N, 4.40%.

 $\frac{3-(3-(4-\text{Phenoxyphenyl})\text{prop-2-enyl})-N-\text{phenyl-2,5-pyrollidinedione 8i} : mp = 132-133 \text{ °C; }^{1}\text{H NMR } \delta (\text{CDCl}_{3})}{2.61-2.73 (m, 1H, H1'), 2.70 (dd, J_{4trans} = 18.2, J_3 = 4.5, H4_{cis}), 2.78-2.87 (m, 1H, H1'), 2.99 (dd, J_{4cis} = 18.2, J_3 = 9.1, H4_{trans}), 3.15 (m, H3), 6.06 (dt, J_{3'} = 15.7, J_{1'} = 7.3, H2'), 6.51 (d, J_{3'} = 15.7, H3'), 6.94-7.02 (m, 4H, H1'), 2.94 (m, 21.5, 2$

ArH), 7.10 (t, 1H, J = 7.3, ArH), 7.24-7.48 (m, 9H, ArH); Anal. calcd. for C₂₅H₂₁NO₃ : C, 78.31%; H, 5.52%; N, 3.65% - Found : C, 77.95%; H, 5.41%; N, 3.72%.

3-(3-(2-(2.4-dichloro-1.3,5-triazin-6-yloxy)phenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione **11** : A mixture of 6-(2-allylphenoxy)-2,4-dichloro-1,3,5-triazine (**10**) (20.0 g, 71 mmol), *N*-phenylmaleimide (14.7 g, 85 mmol), quinol (0.77 g, 7 mmol) and 1,2,4-trichlorobenzene (13.0 g, 71 mmol) was heated under N₂ at 200 °C for 24 h, to yield on cooling a dark glass soluble in methanol. Silica gel column chromatography (eluent: hexane/ethyl acetate) gave three fractions, the first (*ca.* 14 g) contained unreacted triazine (**10**) and 1,2,4-trichlorobenzene, the second (7.7 g) contained crude cinnamyl product, and the third (*ca.* 19 g) was a resinous material. The second fraction containing the product was subjected to further column chromatography (eluent: hexane) to yield 3-(3-(2-(2,4-dichloro-1,3,5-triazin-6-yloxy)phenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione (**11**) (3.6 g 11%) as a slightly orange solid; a sample was recrystallised from hexane to yield a colourless solid: mp 68-70 °C; ¹H NMR δ (acetone-*d*₆) 2.55-2.68 (m, 2H, H4_{*cis*} and H1'), 2.77-2.81 (m, 1H, H1'), 2.99 (dd, 1H, *J* = 18.0 and 9.2 Hz, H4_{*trans*}), 3.22 (m, 1H, H3), 6.46 (dt, 1H, *J* = 15.6 and 7.2 Hz, H2'), 6.69 (d, 1H, *J* = 15.6 Hz, H3'), 7.27-7.48 (m, 8H, ArH), 7.73 (d, 1H, *J* = 4.0 Hz, ArH). Anal. Calcd for C₂₂H₁₆Cl₂N₄O₃: C, 58.14; H, 3.55; N, 12.34. Found: C, 58.27; H, 3.59; N, 12.37.

Ene Reaction of Tris(allylphenoxy)triazine 12.

A mixture of 2,4,6-*tris*-(2-allylphenoxy)-1,3,5-triazine (**12**) (5.5g, 11.5 mmol), *N*-phenylmaleimide (6.6 g, 37.7 mmol), quinol (0.25 g, 2.3 mmol) and 1,2,4-trichlorobenzene (2.1 g, 11.5 mmol) was heated under N₂ at 200 °C for 24 h, to yield on cooling a dark glass. Tlc and ¹H NMR showed the crude product to be a complex mixture which after silica gel column chromatography (eluent: hexane/ethyl acetate) gave five fractions. The first (*ca.* 2.3 g) contained unreacted triazine (**12**) (0.72 mmol, 6%), 2-allylphenol (**1j**) (3.3 mmol, 10%) and 1,2,4-trichlorobenzene (5.4 mmol, 47%) (identified by tlc and ¹H NMR and quantified by ¹H NMR). The second (1.2 g) contained a complex mixture of products (tlc) which could not be separated. The third fraction (*ca.* 0.9 g) was a solid containing one major product by tlc; this solid was recrystallised from dichloromethane-hexane to yield 3-(3-(2-hydroxyphenyl))prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione (**8j**) (350 mg, 1.14 mmol, 3.3%) as a white solid: mp 141-3 °C; ¹H NMR δ (acetone-*d*₆) 2.63-2.75 (m, 1H, H1'), 2.75 (dd, 1 H, *J* = 19.0 and 6.0 Hz, H4_{*cis*}), 2.75-2.85 (m, 1H, H1'), 3.03 (dd, 1H, *J* = 18.0 and 9.2 Hz, H4_{*trans*}), 3.26 (m, 1H, H3), 6.34 (dt, 1H, *J* = 15.9 and 7.3 Hz, H2'), 6.77-6.90 (m, 3H, H3' and ArH), 7.07 (t, 1H, ArH), 7.29-7.48 (m, 6H, ArH), 8.47 (s, 1H, OH); ¹³C NMR δ (acetone-*d*₆) 34.4 (C4), 35.4 (C1'), 40.6 (C3), 116.5, 120.5, 125.1, 126.3, 127.7, 127.8, 128.8, 129.1, 129.2, 129.45, 134.0, 155.2 (12C, C2', C3' and ArC), 176.1 (C5), 179.15 (C2). Anal. Calcd for C₁₉H₁₇NO₃: C, 74.24; H, 5.58; N, 4.56. Found: C, 73.94; H, 5.47; N, 4.54.

The fourth fraction (*ca.* 0.3 g) was also a mixture (tlc) and yielded no pure material. The final fraction (*ca.* 9.2 g) contained only material showing a broad aromatic signal in the ¹H NMR.

The reaction was repeated with 11.5 g of **12** and yielded a crude product similar to that above (¹H NMR). Silica gel column chromatography yielded initial, third and final fractions as before. The second fraction was washed with dilute aqueous NaOH solution until tlc showed it to be free of the phenol (**8**j) and subjected to further column chromatography (eluent: hexane/ethyl acetate) to yield the mono-adduct *N*-phenyl-3-(-3-(2-(4,6-di(2-(prop-2-enyl)phenoxy)-1,3,5-triazin-2-yloxy)phenyl)prop-2-enyl)-2,5-pyrollidinedione (**13**) (1.07 g, 7%) as an oil. A sample was purified to a single peak by silica HPLC (eluent: chloroform) to give a solid: mp 52-4 $^{\circ}$ C; ¹H NMR δ (acetone-*d*₆) 2.56-2.65 (m, 1H, H1'), 2.61 (dd, 1H, *J* = 17.9 and 5.0 Hz, H4_{cis}), 2.78-2.86 (m, 1H, H1'), 2.99 (dd, 1H, *J* = 18.0 and 9.3 Hz, H4_{trans}), 3.21 (m, 1H, H3), 3.25 (d, 4H, *J* = 6.7 Hz, H1"), 4.93-4.99 (m, 4H, H3"), 5.76-5.90 (m, 2H, H2"), 6.37 (dt, 1H, *J* = 15.9 and 7.1 Hz, H2'), 6.59 (d, 1H, *J* = 15.9 Hz, H3'), 7.09-7.48 (m, 16H, ArH), 7.56 (d, 1H, *J* = 7.2 Hz, ArH); ¹³C NMR δ (acetone-*d*₆) 34.6 (C4), 35.0 (C1"), 35.4 (C1'), 40.7 (C3), 116.6 (C3"), 123.2, 123.4, 127.15, 127.2, 127.8, 127.9, 128.3, 128.9, 129.2, 129.6, 130.7, 131.2, 132.8, 134.0, 149.9, 151.1, 174.8, (17C, C3', ArH and triazinyl C), 130.1 (C2'), 137.0 (C2"), 176.1 (C5), 179.0 (C2) ¹; HRMS(FAB). Calcd for C₄₀H₃₄N₄O₅ 650.2529. Found 650.2537. LRMS(FAB) *m/z* 650 (98), 476 (100), 115 (60). Anal. Calcd: C, 73.82; H, 5.27; N, 8.61. Found: C, 73.24; H, 5.01; N, 8.49.

The fourth fraction (*ca.* 3 g) although homogenous by ¹H NMR could not be obtained analytically pure; a small sample was recrystallised from ethanol and purified twice to a single peak by silica HPLC (eluent: chloroform) to yield the di-adduct (2-(4-(2-(prop-2-enyl)phenoxy)-1,3,5,-triazine-2,6-diyl)dioxy)*bis-N*-phenyl-3-(3-phenylprop-2-enyl)-2,5-pyrollidinedione (14) (60 mg, 0.3%) as an oil: ¹H NMR δ (acetone-*d*₆) 2.53-2.63 (m, 2H, H1'), 2.59 (dd, 2H, *J* = 18.0 and 4.8 Hz, H4_{*cis*}), 2.75-2.82 (m, 2H, H1'), 2.96 (dd, 2H, *J* = 18.0 and 9.2 Hz, H4_{*trans*}), 3.18 (m, 2H, H3), 3.25 (m, 2H, *J* = 6.4 Hz, H1"), 4.93-4.98 (m, 2H, H3"), 5.61-5.84 (m, 1H, H2"), 6.35 (dt, 2H, *J* = 15.8 and 7.1 Hz, H2'), 6.59 (d, 2H, *J* = 15.9 Hz, H3'), 7.09-7.48 (m, 20H, ArH), 7.56 (d, 2H, *J* = 7.1 Hz, ArH); ¹³C NMR δ (acetone-*d*₆) 34.6 (C4), 35.0 (C1"), 35.3 (C1'), 40.7 (C3), 116.6 (C3"), 123.2, 123.5, 127.1, 127.2, 127.8, 127.9, 128.3, 128.9, 129.2, 129.6, 130.65, 131.2, 132.8, 134.0, 149.9, 151.1, 174.8 (17C, C3', ArC and triazinyl C), 130.1 (C2'), 137.0 (C2"), 176.2 (C5), 179.1 (C2) ¹. LRMS(FAB) 823 (58), 649 (100).

Reactivity Studies.

The alkene (allyl compound), typically 1.3 - 8.4 mmol, equimolar enophile, equimolar solvent (1,2,4-trichlorobenzene) and 10 mole% quinol were placed in a 25 mL round-bottomed flask fitted with a reflux

¹ The NMR assignments for 13 and 14 are based on DEPT and ¹H, ¹H and ¹H, ¹³C COSY experiments (see analysis for 8b), although the C3' signal could not be unambiguously assigned. For both compound 13 and 14 the two nominally unique triazine carbons appeared to give only coincident signals and one aryl or alkenyl CH carbon signal is missing amongst the others.

condenser, warmed gently to effect dissolution and placed in an oil bath heated to between 186 and 198 °C; the reactions were *not* under an N₂ atmosphere. The reactions were analysed by removing aliquots (typically 75 mg) at t = 0 m and again at t = 180 m; during this period, all the reactions darkened and became more viscous, but (except for those using maleimide (3) as enophile) remained homogenous and showed no apparent loss of overall volume. A known weight of dioxan (typically 15 mg), as a standard, was added to the weighed sample aliquots followed by acetone- d_6 which dissolved all the sample, and the amounts of the reaction components were determined by integration of suitable peaks in the ¹H NMR. From this the amount of each component in the overall reaction mixture, assuming no overall loss of material, was calculated; the fractional or % yields quoted for products are based on the theoretical yields assuming complete conversion of triazine. In each case a simultaneous, but separate, duplicate was run in the same bath, and where different reactions were to be directly compared, they were carried out simultaneously in the same bath.

In the case of the *tris*-(2-allylphenoxy)triazine (12) a similar method was used, except that 10 mmol of triazine, 10 mmol of solvent, 30 mmol (3 equivalents) of enophile and 1 mmol of quinol at 201 °C were used. Aliquots were taken at t = 0 and 30 m, and thereafter every 15 m up to 4 h.

The quoted bath temperatures were steady over the period of the reaction to within ± 1 °C, and the uncertainties in the fractional yields are estimated to be *ca*. $\pm 10\%$ for values 0.5-1.0, but up to $\pm 20\%$ for values below 0.5.

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