Pergamon

Tetrahedron, Vol. 53, No. 39, pp. 13473-13494, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00856-9

The Ene Reaction between Maleimides and Allyl-substituted Aromatics

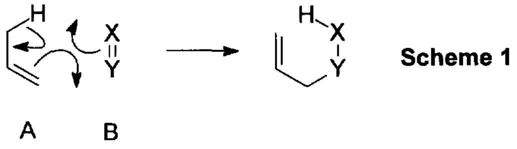
Ian D. Cunningham,* Andrew Brownhill, Ian Hamerton, and Brendan J. Howlin

Department of Chemistry, University of Surrey, Guildford GU2 5XH, UK

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.

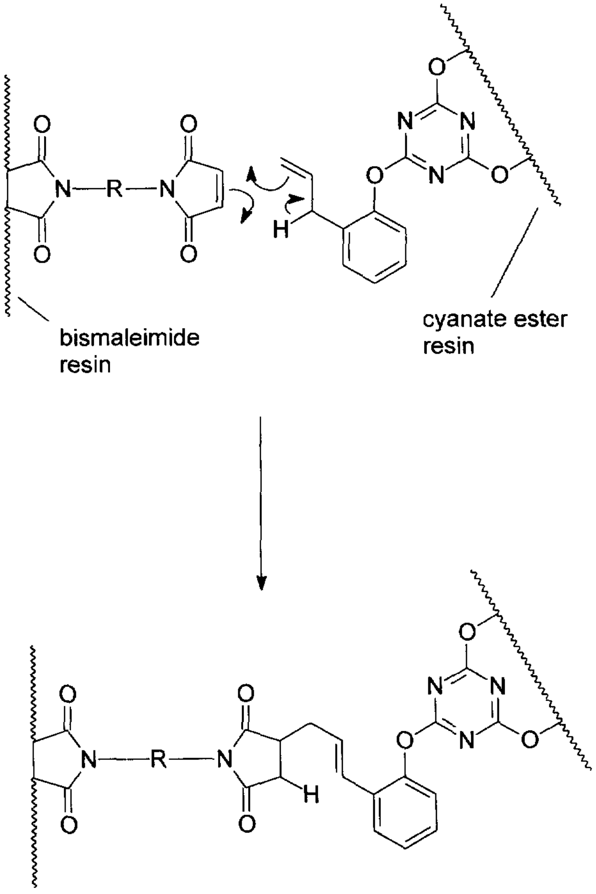
INTRODUCTION

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



Scheme 1

The reaction was first investigated by Alder in 1943,[1] but despite several reviews[2] and a steady flow of new research[3] 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 'enophile' 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 propargyl[2] 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]

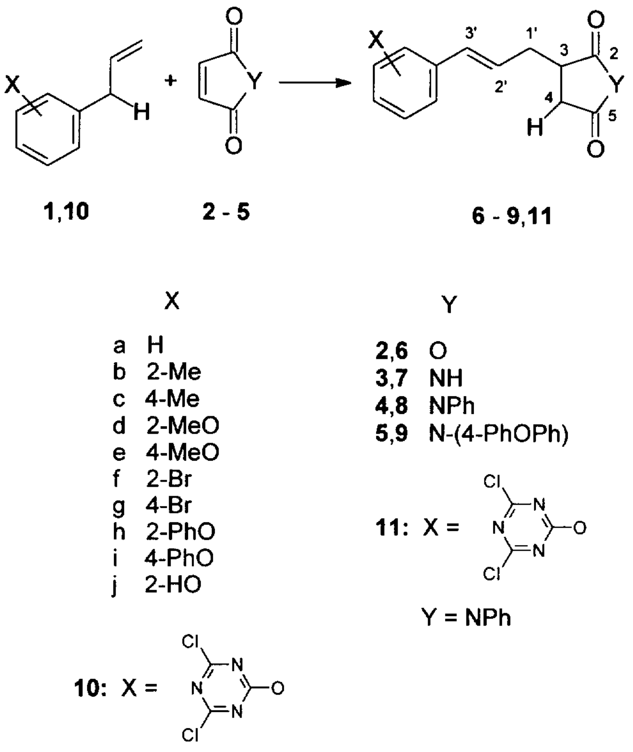
Therefore, following on from our recent study of the Lewis acid-catalysed cyanate ester cyclotrimerisation reaction,[12] we have undertaken a scope and reactivity study of the ene reaction of allyl benzenes (**1**) with maleimides (**3-5**) along with maleic anhydride (**2**). In addition we have studied 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 (2,5-pyrollediones) (**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)-2,5-pyrollidinediones (**7-9**) shown in Scheme 3.

The products were isolated by vacuum distillation in up to 30% yield and were homogenous by ^{1}H NMR. Purification for characterisation was by recystallisation from ethanol-water or by column chromatography (SiO_2) followed by recrystallisation. Product (**6-9**) identities were confirmed by the CHN microanalyses and by comparison of the ^{1}H NMR spectra with those of compounds **6b-9b** (X = 2-CH_3) whose ^{1}H and ^{13}C NMR signals were fully assigned (Table 1) from ^{1}H,^{1}H COSY, ^{1}H,^{13}C COSY and ^{13}C DEPT experiments as well as consideration of δ_H, δ_C and $J_{H,H}$ 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 CH_3, C2' and C3', respectively, from the ^{1}H,^{13}C COSY experiment. The remaining non-methylene carbon signal (DEPT) in the aliphatic region, 40.9 ppm, was assigned to C3 and ^{1}H,^{13}C COSY identified the H3 signal as the 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; this identified the two multiplets as being due to the two H1' protons, and therefore, the double-doublet 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,^{13}C COSY) to the discrete H4 and H1' signals.

Table 1. ^{13}C and ^{1}H NMR Chemical Shifts (ppm, relative to TMS) for 3-(3-(2-Methylphenyl)prop-2-enyl) dihydro-2,5-furandione **6b** and 2,5-pyrollidinediones **7b**, **8b** and **9b** in Acetone-d_6

compd	CH_3	C2	C3	C4	C5	C1'	C2'	C3'	Ar-C [a]
6b	19.9	175.2	41.7	34.2	171.9	34.6	127.5	132.35	126.5, 126.95, 128.3, 131.1, *136.0*, *137.1*
7b	19.9	180.9	42.0	35.0 [b]	177.85	35.5 [b]	128.2	131.8	126.5, 127.0, 128.3, 131.05, *135.9*, *137.2*
8b	19.9	179.2	40.9	34.55	176.2	35.3	128.1	132.0	126.5, 127.0, 127.9, 128.2, 128.9, 129.6, 131.1, *134.1*, *135.9*, *137.3*
9b	19.9	179.3	40.9	34.5	176.3	35.3	128.1	132.0	119.25, 120.2, 124.8, 126.5,127.0, 128.2, *128.9*, 129.45, 131.0, 131.1, *135.9*, *137.3*, *157.7*, *158.0*

compd	CH_3	H3	$H4_{trans}$	$H4_{cis}$	H1'(2H)	H2'	H3'	ArH
6b	2.32 (s)	3.56 (m)	3.25 (dd, J_{4cis} = 18.6, J_3 = 9.6)	2.96 (dd, J_{4trans} = 18.6, J_3 = 6.3)	2.61-2.75 (m, 1H), 2.80-2.90 (m, 1H)	6.13 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.3)	6.82 (d, $J_{2'}$ = 15.7)	7.17 (m, 3H), 7.57 (m, 1H)
7b	2.32 (s)	3.11 (m)	2.89 (dd, J_{4cis} = 18.0, J_3 = 9.2)	2.54 (dd, J_{4trans} = 18.1, J_3 = 4.9)	2.50-2.59 (m, 1H), 2.71-2.80 (m, 1H)	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)
8b	2.33 (s)	3.27 (m)	3.05 (dd, J_{4cis} = 18.0, J_3 = 9.2)	2.73 (dd, J_{4trans} = 18.1, J_3 = 4.8)	2.63-2.73 (m, 1H), 2.82-2.90 (m, 1H)	6.19 (dt, $J_{3'}$ = 15.6, $J_{1'}$ = 7.1)	6.83 (d, $J_{2'}$ = 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} = 18.0, J_3 = 9.2)	2.74 (dd, J_{4trans} = 18.0, J_3 = 4.8)	2.63-2.73 (m, 1H), 2.82-2.93 (m, 1H)	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.

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 ^{1}H 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 ν(C=O) and ν(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 2,5-pyrollidinediones **7b**, **8b** and **9b** (Nujol Mull)

compd	ν(C=O)	ν(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 ^{1}H 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, ^{1}H 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.[¶] 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.

[#] The ^{1}H NMR and ^{13}C NMR spectral data for **6b** in acetone-d_6 are given in Table 1. ^{1}H NMR spectra for compounds **6b** and **6d** in $CDCl_3$ and for **6bA** and **6dA** in acetone-d_6 are given in the experimental.

[¶] 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.

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

	reaction of allylbenzene **1a** 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

A semi-quantitative assessment of reactivity by ^{1}H 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 ^{1}H NMR. As after 24 h, no evidence of *Z*-prop-2-enyl product is observed after 3 h.

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

allylarene	X	% ene **1** unreacted after 3 h	% product formed after 3 h
1a	H	33	16
1b	2-CH_3	39	16
1c	4-CH_3	59	14
1d	2-CH_3O	52	14
1e	4-CH_3O	43	12
1g	4-Br	50	10
1h[a]	2-PhO	44	19
1i	4-PhO	37	7

---

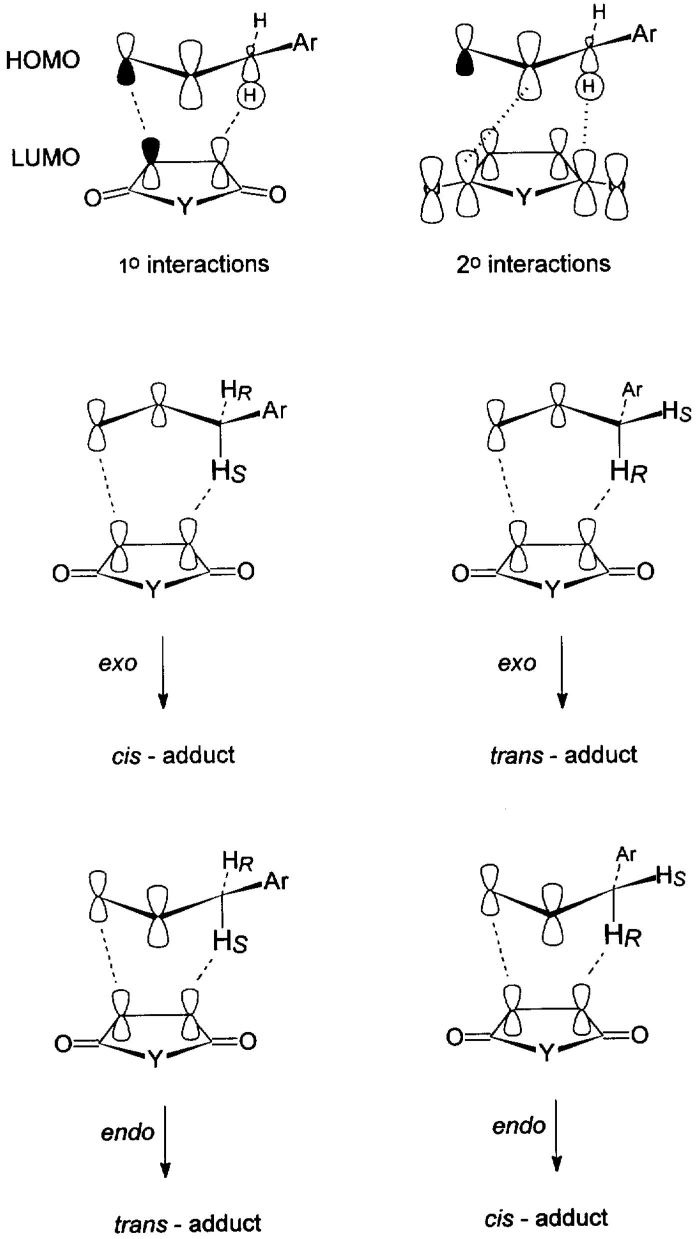
[a] T = 194 °C.

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]-hydrogen-shift involving a H-C-C=C ($2\sigma,2\pi$) 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 maleimide-but-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 ^{1}H 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 (^{1}H 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 ^{13}C and ^{1}H 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 ^{13}C NMR and ^{1}H 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.[¶] 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 ^{1}H and ^{13}C NMR (see experimental) which were almost identical to those of **13** except that the relative allyl/propenylpyrollidenedione intensities/areas were *ca.* 1:2 in this case. A material showing only a broad aromatic signal in its ^{1}H 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 ^{1}H 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.

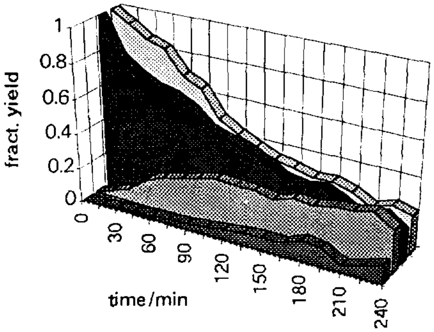
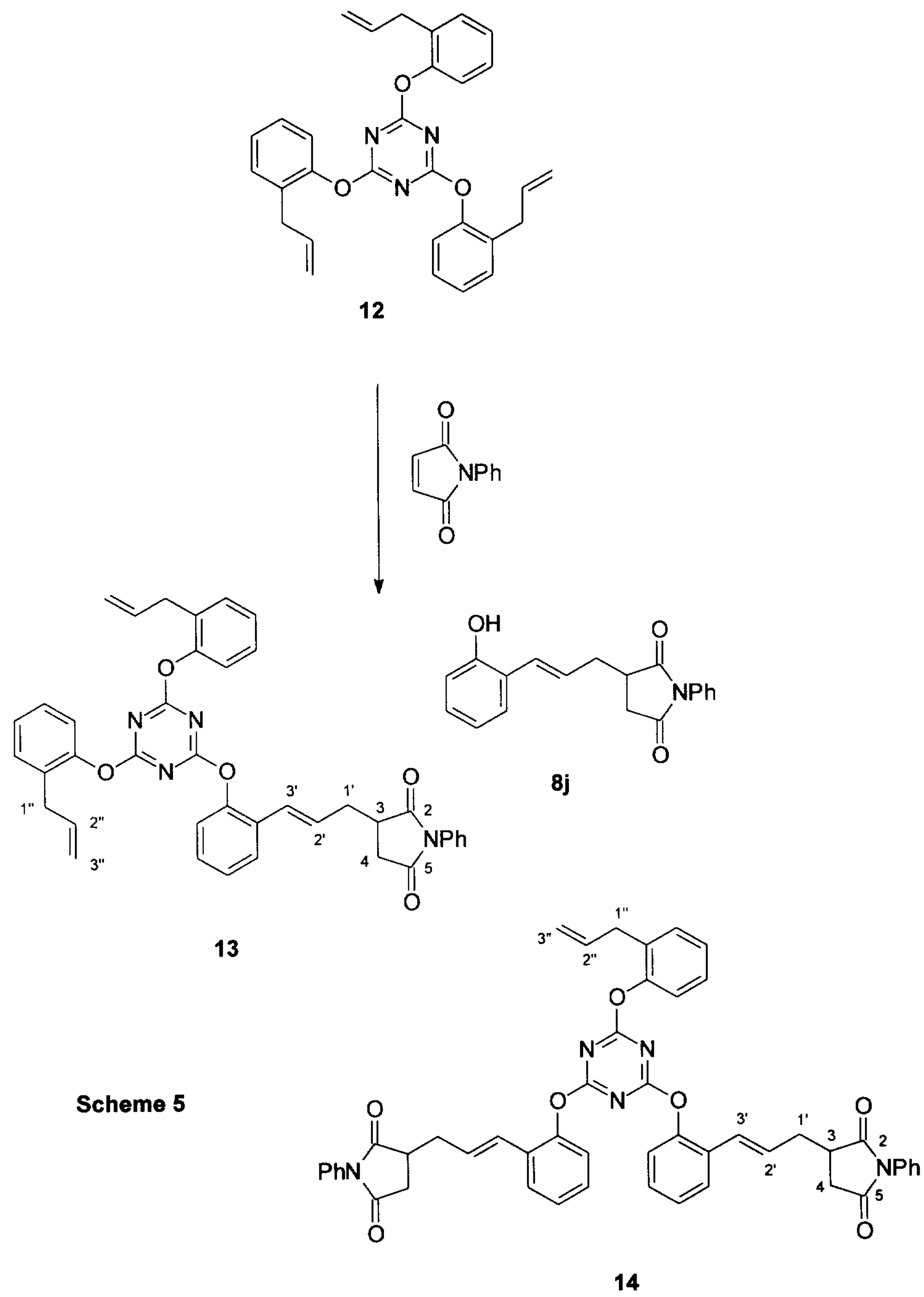


Figure 1. Variation of Reagents and Products with Time for Reaction of *Tris*-2,4,6-(2-allylphenoxy)triazine (**12**) with *N*-Phenylmaleimide (**4**) in 1,2,4-Trichlorobenzene at 201°C. Compounds from rear to front are : triazine **12**, *N*-phenylmaleimide **4**, mono-adduct **13** and di-adduct **14**.

[¶] The NMR assignments for **13** and **14** are based on DEPT and $^{1}H,^{1}H$ and $^{1}H,^{13}C$ 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.



Scheme 5

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 (^{1}H 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 ^{1}H 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 (^{1}H NMR) homogenous materials, unless otherwise stated. Microanalyses were carried out on a Leeman Labs Inc. CE 440 elemental analyser. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 MHz spectrometer operating at 75.47 MHz for ^{13}C; the reference was TMS.

Materials.

Maleic anhydride (**2**), maleimide (**3**), *N*-phenylmaleimide (**4**), 4-phenoxyaniline, allylbenzene (**1a**), 4-allylanisole (**1e**), 2-allylphenol (**1j**), 2-bromoiodobenzene, 2-bromotoluene, 4-bromotoluene, 1,4-dibromobenzene, 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.

Allyl Compounds.

Literature methods were used for the preparations of: *N*-(4-phenoxyphenyl)maleimide (**5**) from 4-phenoxyaniline and maleic anhydride[15] 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 4-bromotoluene, respectively;[17] 4-allyl-1-bromobenzene (**1g**) from 1,4-dibromobenzene;[18] 2-allyl-1-bromobenzene (**1f**) from 2-bromo-1-iodobenzene;[19] 4-allyl-1-phenoxybenzene (**1i**) from 4-bromodiphenyl ether;[20] and 2-allyl-1-phenoxybenzene (**1h**) from 2-bromodiphenyl ether.[21] The 2-bromodiphenyl ether was prepared from diphenyl ether *via* 2-aminodiphenyl ether[22] 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 $TiCl_4$-catalysed cyclotrimerisation of 2-allylphenyl cyanate prepared from cyanogen bromide and 2-allylphenol as described previously.[12]

6-(2-Allylphenoxy)-2,4-dichloro-1,3,5-triazine **10** : To a solution of cyanuric chloride (30.0 g, 162 mmol) in 200 mL of $CHCl_3$, 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 $CHCl_3$ (2 x 50 mL). The organic layers were combined, dried ($MgSO_4$), 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_9H_9Cl_2N_3O$: 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 1,2,4-trichlorobenzene (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 ($CDCl_3$) 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).

3-(3-Phenylprop-2-enyl)-2,5-pyrollidinedione **7a** : mp = 118-119 °C; ^{1}H NMR δ (CDCl$_3$) 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 $C_{13}H_{13}NO_2$: C, 72.54%; H, 6.09%; N, 6.51% - Found : C, 72.36%; H, 6.02%; N, 6.41%.

N-Phenyl-3-(3-phenylprop-2-enyl)-2,5-pyrollidinedione **8a** : mp = 118.5-119.5 °C; ^{1}H NMR δ (CDCl$_3$) 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 $C_{19}H_{17}NO_2$: C, 78.33%; H, 5.88%; N, 4.81% - Found : C, 78.17%; H, 5.85%; N, 4.78%.

N-(-4-Phenoxyphenyl)-3-(3-phenylprop-2-enyl)-2,5-pyrollidinedioneand **9a** : mp = 114.5-115.5 °C; ^{1}H NMR δ (CDCl$_3$) 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 $C_{25}H_{21}NO_3$: C, 78.31%; H, 5.52%; N, 3.65% - Found : C, 78.34%; H, 5.48%; N, 3.69%.

3-(3-(2-Methylphenyl)prop-2-enyl)dihydro-2,5-furandione **6b** : mp = 72-74 °C; ^{1}H NMR δ (CDCl$_3$) 2.33 (s, CH$_3$), 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; ^{1}H NMR δ (acetone-d_6) 2.32 (s, CH$_3$), 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, CO$_2$H); Anal. calcd. for $C_{14}H_{16}O_4$: 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; ^{1}H NMR δ (CDCl$_3$) 2.33 (s, CH$_3$), 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 $C_{14}H_{15}NO_2$: C, 73.07%; H, 6.60%; N, 6.04% - Found : C, 73.34%; H, 6.59%; N, 6.11%.

3-(3-(2-Methylphenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione **8b** : mp = 100-101 °C; ^{1}H NMR δ ($CDCl_3$) 2.33 (s, CH_3), 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 $C_{20}H_{19}NO_2$: C, 78.66%; H, 6.27%; N, 4.59% - Found : C, 78.26%; H, 6.15%; N, 4.56%.

3-(3-(2-Methylphenyl)prop-2-enyl)-*N*-(4-phenoxyphenyl)-2,5-pyrollidinedioneand **9b** : mp = 131-133 °C; ^{1}H NMR δ ($CDCl_3$) 2.33 (s, CH_3), 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%.

3-(3-(4-Methylphenyl)prop-2-enyl)dihydro-2,5-furandione **6c** : mp = 95-96 °C; ^{1}H NMR δ ($CDCl_3$) 2.34 (s, CH_3), 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 $C_{14}H_{14}O_3$: C, 73.03%; H, 6.13%; - Found : C, 72.74%; H, 6.06%.

3-(3-(4-Methylphenyl)prop-2-enyl)-2,5-pyrollidinedione **7c** : mp = 166-167 °C; ^{1}H NMR δ (acetone-d_6) 2.29 (s, CH_3), 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 $C_{14}H_{15}NO_2$: C, 73.34%; H, 6.59%; N, 6.11% - Found : C, 73.17%; H, 6.58%; N, 6.02%.

3-(3-(4-Methylphenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione **8c** : mp = 137-138 °C; ^{1}H NMR δ ($CDCl_3$) 2.33 (s, CH_3), 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 $C_{20}H_{19}NO_2$: C, 78.66%; H, 6.27%; N, 4.59% - Found : C, 78.69%; H, 6.23%; N, 4.66%.

3-(3-(4-Methylphenyl)prop-2-enyl)-*N*-(4-phenoxyphenyl)-2,5-pyrollidinedioneand **9c** : mp = 143-144 °C; ^{1}H NMR δ ($CDCl_3$) 2.33 (s, CH_3), 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 $C_{26}H_{23}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 3.63 (s, CH_3O), 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; ^{1}H NMR δ (acetone-d_6) 3.84 (s, CH_3O), 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, CO_2H); Anal. calcd. for $C_{14}H_{16}O_5$: 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; ^{1}H NMR δ ($CDCl_3$) 3.80 (s, CH_3O), 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 $C_{14}H_{15}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 3.84 (s, CH_3O), 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 $C_{20}H_{19}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 3.83 (s, CH_3O), 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 $C_{26}H_{23}NO_4$: 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 6e : mp = 104.5-105.5 °C; ^{1}H NMR δ ($CDCl_3$) 3.76 (s, CH_3O), 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 $C_{14}H_{14}O_4$: 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; ^{1}H NMR δ ($CDCl_3$) 3.80 (s, CH_3O), 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 $C_{14}H_{15}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 3.80 (s, CH_3O), 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 $C_{20}H_{19}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 3.80 (s, CH_3O), 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 $C_{26}H_{23}NO_4$: C, 75.53%; H, 5.61%; N, 3.39% - Found : C, 75.29%; H, 5.49%; N, 3.37%.

3-(3-(4-Bromophenyl)prop-2-enyl)dihydro-2,5-furandione 6g : mp = 105-107 °C; ^{1}H NMR δ ($CDCl_3$) 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 $C_{13}H_{11}O_3Br$: C, 52.91%; H, 3.76% - Found : C, 52.89%; H, 3.72%.

3-(3-(4-Bromophenyl)prop-2-enyl)-2,5-pyrollidinedione 7g : A solid homogenous by ^{1}H NMR and which melted over a range of 165 to *ca.* 175 °C; ^{1}H NMR δ ($CDCl_3$) 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).

3-(3-(4-Bromophenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione **8g** : mp = 124-125 °C; ^{1}H NMR δ ($CDCl_3$) 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 $C_{19}H_{16}NO_2Br$: 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 ^{1}H NMR, but was not fully characterised; ^{1}H NMR δ ($CDCl_3$) 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; ^{1}H NMR δ ($CDCl_3$) 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 $C_{25}H_{21}NO_3$: 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; ^{1}H NMR δ ($CDCl_3$) 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 $C_{19}H_{16}O_4$: 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; ^{1}H NMR δ ($CDCl_3$) 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 $C_{19}H_{17}NO_3$: C, 74.25%; H, 5.58%; N, 4.56% - Found : C, 73.53%; H, 5.51%; N, 4.40%.

3-(3-(4-Phenoxyphenyl)prop-2-enyl)-*N*-phenyl-2,5-pyrollidinedione **8i** : mp = 132-133 °C; ^{1}H NMR δ ($CDCl_3$) 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, ArH), 7.10 (t, 1H, J = 7.3, ArH), 7.24-7.48 (m, 9H, ArH); Anal. calcd. for $C_{25}H_{21}NO_3$: 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 N_2 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; ^{1}H 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 $C_{22}H_{16}Cl_2N_4O_3$: 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 N_2 at 200 °C for 24 h, to yield on cooling a dark glass. Tlc and ^{1}H 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 ^{1}H NMR and quantified by ^{1}H 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; ^{1}H 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); ^{13}C 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 $C_{19}H_{17}NO_3$: 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 ^{1}H NMR.

The reaction was repeated with 11.5 g of **12** and yielded a crude product similar to that above (^{1}H 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 (**8j**) 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 °C; ^{1}H 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); ^{13}C 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 $C_{40}H_{34}N_4O_5$ 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 ^{1}H 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: ^{1}H 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); ^{13}C 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 ^{1}H,^{1}H and ^{1}H,^{13}C 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 N_2 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 ^{1}H 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.* ±10% for values 0.5-1.0, but up to ±20% for values below 0.5.

ACKNOWLEDGEMENTS

We are grateful to the EPSRC for a research grant (GR/H29339) and to Mr. J. Bloxsidge for running some NMR spectra.

REFERENCES

1. Alder, K.; Pascher, F.; Schmitz, A. *Chem. Ber.* **1943**, *76B*, 27.
2. Hoffmann, H. M. R. *Angew. Chem. Internat. Edit.* **1969**, *8*, 556. (b) Keung, E. C.; Alper, H. *J. Chem. Ed.* **1972**, *49*, 97. (c) Borzilleri, R. M.; Weinreb, S. M. *Synthesis* **1995**, 347.
3. Yliniemelä, A.; Konschin, H.; Pietilä, L.-O.; Teleman, O. *J. Mol. Struct.* **1995**, *334*, 173. (b) Yliniemelä, A.; Konschin, H.; Neagu, C.; Pajunen, A.; Hase, T.; Brunow, G.; Teleman, O. *J. Am. Chem. Soc.* **1995**, *117*, 5120. (c) Desimoni, G.; Faita, G.; Righetti, P. P.; Vietti, F. *Heterocycles* **1995**, *40*, 817. (d) Jin, J.; Smith, D. T.; Weinreb, S. M. *J. Org. Chem.* **1995**, *60*, 5366. (e) Meyer, C.; Marek, I.; Courtemanche, G.; Normant, J.-F. *J. Org. Chem.* **1995**, *60*, 863. (f) Billups, W. E.; Luo, W.; Lee, G.-A.; Chee, J. *J. Org. Chem.* **1996**, *61*, 764.

4. See for example some recent general reviews: (a) Wender, P. A. (Ed) *Chem. Rev.* **1996**, *96*, 49, 137, 167. (b) Cunningham, I. D. *Annu. Rep. Prog. Chem., Sect. B. Org. Chem* **1995**, *92*, 25.
5. Garsky, V.; Koster, D. F.; Arnold, R. T. *J. Am. Chem. Soc.* **1974**, *96*, 4207. (b) Hill, R. K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1964**, *86*, 965.
6. Snider, B. B.; Ron, E. *J. Am,.Chem. Soc.* 1985, *107*, 8160. (b) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.
7. Jin, J.; Smith, D. T.; Weinreb, S. M. *J. Org. Chem.* **1995**, *60*, 5366.
8. Barton, J. M.; Hamerton, I.; Jones, J. R. *Polymer International* **1992**, *29*, 145. (b) Hamerton, I. (Ed) *Chemistry and Technology of Cyanate Ester Resins*, Blackie, Glasgow, **1994**. (c) Hamerton, I.; Hay, J. N. *Trends in Polymer Science*, in the press. (d) Chaplin. A; Hamerton, I; Howlin, B. J.; Barton, J. M. *Macromolecules* **1994**, *28*, 1043. (e) Barton, J. M.; Hamerton, I; Jones, J. R.; Stedman, J. C. *Polymer* **1996**, *37*, 4519. (f) Hamerton, I. *High Performance Polymers* **1996**, *8*, 83.
9. Zahir, S.; Chaudhari, M. A.; King, J. *Makromol. Chem. Macromol. Symp.* **1989**, *25*, 141. (b) Carduner, K. R. ; Chatta, M. S. *Cross-Linked Polymers*, ACS Symp. Series, Washington DC, USA, **1988**, p. 379.
10. Isaacs, N. S. *Physical Organic Chemistry*, Longman, Harlow, **1995**, p. 713.
11. For example, while maleic anhydride reacts with 1-oxa[4.4.4]propella-5,7-diene under pressure, *N*-phenylmaleimide fails to react under the same conditions. Paquette, L. A.; Branan, B. N.; Rogers, R. D. *J. Org. Chem.* **1995**, *60*, 1852.
12. Cunningham, I. D.; Brownhill, A.; Hamerton, I.; Howlin, B. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1937.
13. Benn, F. R.; Dwyer, J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 533.
14. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, **1976**.
15. Barton, J.; Hamerton, I.; Thompson, C. P. *Polym. Bull.* **1993**, *30*, 521.
16. Adams, R.; Rindfusz, R. E. *J. Am. Chem. Soc.* **1919**, *41*, 648.
17. Hurd, C. D.; Bollman, H. T. *J. Am. Chem. Soc.* **1934**, *56*, 447.
18. Jones, L. B.; Foster, J. P. *J. Org. Chem.* **1970**, *35*, 1777.
19. Camaggi, C. M.; Leardini, R.; Zanirato, P. *J. Org. Chem.* **1977**, *42*, 1570.
20. Low, T. P.; Lee, K. H. *J. Chem. Soc., B* **1970**, 535.
21. Fujimoto, Y.; Tamada, T. *Brit.* 1,478,108; *Ger Offen.* 2,630,107.
22. Suter, C. M. *J. Am. Chem. Soc.* **1929**, *51*, 2581.
23. Sax, K. J.; Saari, W. S.; Mahoney, C. L.; Gordon, J. M. *J. Org. Chem.* **1960**, *25*, 1590.

(Received in UK 14 *July* 1997; *accepted* 24 *July* 1997)