Diels–Alder reactions of *N*-sulfonyl substituted aza-*ortho*-xylylenes generated from the corresponding 1,4-dihydro-2*H*-3,1-benzoxazin-2-one derivatives

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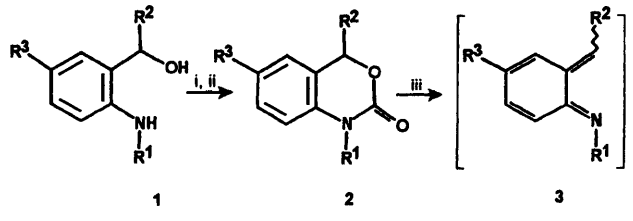
***N*-Tosyl- and *N*-alkylidene-sulfonyl substituted 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones 2c–g easily undergo thermal carbon dioxide extrusion leading to the aza-*ortho*-xylylenes 3c–g. The intermediates 3c,d can be trapped by electron-poor ethylenic and acetylenic dienophiles, giving tetrahydroquinoline and quinoline derivatives. The reactions of 2c with non-symmetrical dienophiles are completely regioselective. *N*-Alkylidenesulfonyl substituted aza-*ortho*-xylylenes 3f–g undergo intramolecular Diels–Alder reactions leading to the tricyclic compounds 10 and 11, while the aza-*ortho*-xylylene generated from 4-(hex-5-enyl)-*N*-(4-methylphenylsulfonyl)-1,4-tetrahydro-2*H*-3,1-benzoxazin-2-one undergoes a [1,5] hydrogen shift leading to *N*-[2-(1*E*)-hepta-1,6-dien-1-ylphenyl]-4-methylbenzenesulfonamide.**

Introduction

During our work on the reactivity of *N*-phenylsulfonyl substituted 1-azabuta-1,3-dienes as precursors of heterocyclic systems,[1] we considered the *N*-tosyl- and *N*-alkylidene-sulfonyl substituted 6-methylenecyclohexa-2,4-dienylideneamines **3c–g** (Scheme 1) as active intermediates. These systems, a class of



1 2 3

a $R^1 = H$, $R^2 = H$, $R^3 = H$
b $R^1 = Me$, $R^2 = H$, $R^3 = H$
c $R^1 = Tos$, $R^2 = H$, $R^3 = H$
d $R^1 = Tos$, $R^2 = Ph$, $R^3 = Cl$
e $R^1 = Tos$, $R^2 = [CH_2]_4CH{=}CH_2$, $R^3 = H$
f $R^1 = SO_2[CH_2]_2CH{=}CH_2$, $R^2 = H$, $R^3 = H$
g $R^1 = SO_2[CH_2]_3CH{=}CH_2$, $R^2 = H$, $R^3 = H$

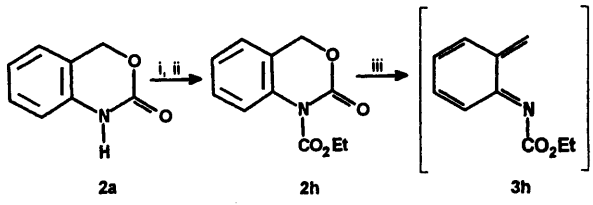
Scheme 1 *Reagents and conditions:* i, BuLi, THF; ii, $COCl_2$; iii, 1,2,4-trichlorobenzene

aza-*ortho*-xylylenes, are used as such in the synthesis of tetrahydroquinoline and quinoline derivatives and polycondensed heterocycles through intermolecular and intramolecular Diels–Alder reactions.

The most widely used routes to aza-*ortho*-xylylenes are flash vacuum pyrolysis (FVP) of *ortho*-aminobenzyl alcohols and *N*-alkyl substituted 3,1-benzoxazin-2-one derivatives,[2,3] thermal ring-cleavage of 2-azidoindoles,[4] fluoride ion-induced 1,4-elimination in *o*-[(trimethylsilyl)alkylamino]benzyl(trimethyl)-ammonium halides[5] and photochemical and thermal sulfur dioxide extrusion from 2,1-benzisothiazoline 2,2-dioxides.[6,7]

Of these precursors the 3,1-benzoxazin-2-one derivatives have been studied little, although upon carbon dioxide (CO_2) extrusion by FVP they are reported to generate the corresponding aza-*ortho*-xylylenes which, depending on the substituent bound to the nitrogen atom (Ph, alkyl, alkenyl), can undergo 6π electrocyclization, [1,5] hydrogen shift and intramolecular cycloaddition respectively.[3a] As far as we know, no intermolecular cycloaddition has been reported with aza-*ortho*-xylylenes from 3,1-benzoxazin-2-one derivatives. To generate the aza-*ortho*-xylylenes **3c–g** we used **2c–g** as precursors, with the expectation that 3,1-benzoxazin-2-ones *N*-substituted with an electron-withdrawing group would release carbon dioxide more easily. The intermediates **3c–g** generated under milder conditions could undergo both inter- and intramolecular cycloadditions more easily.

To check how the substituent bound to the nitrogen atom affected the ability of the corresponding 3,1-benzoxazin-2-one derivatives to undergo CO_2 extrusion, we designed a comparative study employing also the *N*-methyl- and the *N*-ethoxy-carbonyl substituted 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones **2b** (Scheme 1) and **2h** (Scheme 2).



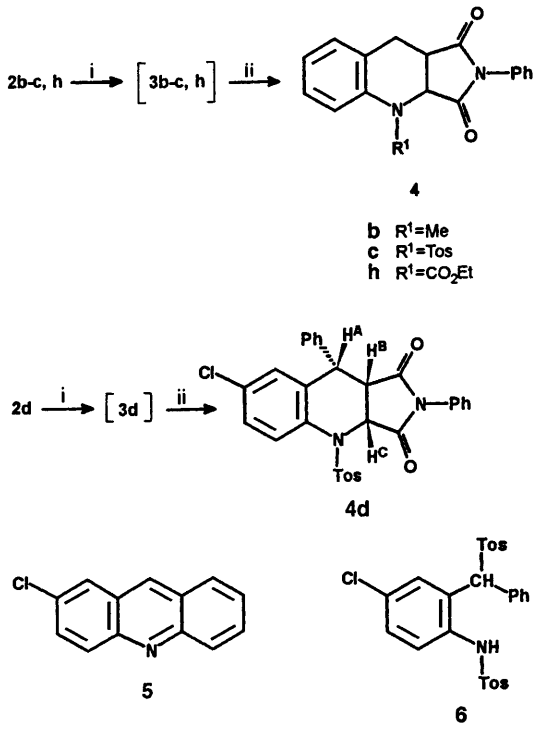
2a 2h 3h

Scheme 2 *Reagents and conditions:* i, NaH, DMI; ii, $ClCO_2Et$; iii, 1,2,4-trichlorobenzene, reflux

Results and discussion

The general synthetic route for easy access to **2b–g** required the corresponding *N*-substituted 2-aminobenzyl alcohols **1b–g** (Scheme 1). They were synthesized by treatment of the corresponding 2-aminobenzyl alcohols with the appropriate sulfonyl chlorides in chloroform using pyridine as a base. Compound **1e** was obtained by addition of the hex-5-enyl

Grignard reagent to the *N*-(2-formylphenyl)-4-methylbenzenesulfonamide in tetrahydrofuran (THF). The bis-anions of **1b–g** prepared with BuLi in THF at −70 °C were treated with phosgene to afford **2b–g** in good yields (Table 1). This synthetic route was not useful for preparing **2h**, which, however, was obtained in a satisfactory yield (Table 1) by treating the anion of 3,1-benzoxazin-2-one **2a** [NaH, 1,3-dimethylimidazolidin-2-one (DMI)] with ethyl chloroformate (Scheme 2). When weaker bases were used, **2h** failed to form and starting material was recovered quantitatively. Compounds **2b–d** and **2h** when heated in 1,2,4-trichlorobenzene at reflux in the presence of the reactive dienophile *N*-phenylmaleimide gave the expected cycloadducts **4b–d,h** after 5–15 h in yields of 16–47% (see Scheme 3 and



Scheme 3 *Reagents and conditions:* i, 1,2,4-trichlorobenzene, reflux; ii, *N*-phenylmaleimide

Tables 2 and 3). The formation of compounds **4b–d,h** is explicable only in terms of CO_2 extrusion from compounds **2b–d,h** to give **3b–d,h** and trapping of the latter by the dienophile. Formation of the adduct **4d** (Scheme 3) is consistent with *endo*-addition of the dienophile to the (*E*)-aza-*ortho*-xylylene **3d**. The assigned stereochemistry was derived initially from comparison of the ^{1}H NMR coupling constants (J_{AB} 6.5 Hz and J_{BC} 9 Hz) (Table 3) of **4d** with those of reported and related *endo*-cycloadducts;[8] the assignment was supported by 2D NOESY experiments which confirmed the *cis* configuration of H^A, H^B and H^C.

Thermolysis of **2d** and *N*-phenylmaleimide gave 2-chloroacridine **5** (12%) and compound **6** (3%) (Scheme 3). Compound **5** arises by 6π electrocyclization of **3d** in the *Z* configuration and subsequent elimination of toluenesulfinic acid; compound **6** arises by addition of toluenesulfinic acid to **3d**. Compound **2d** when heated in the absence of the dienophile gave a mixture of **5** (20%) and **6** (16%).†

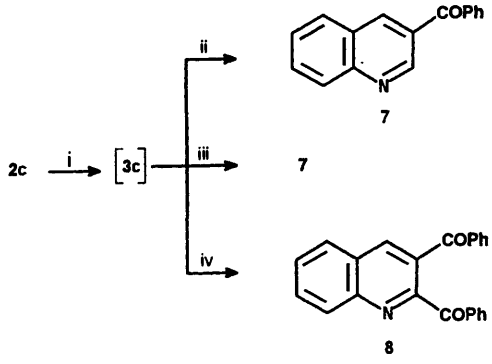
A comparison of thermolysis data (Table 2) shows that 3,1-benzoxazin-2-one derivatives *N*-substituted with an electron-withdrawing group **2c,d,h** release carbon dioxide more easily than **2b**. *N*-Tosyl substituted 3,1-benzoxazin-2-ones, **2c** and **2d** undergo complete CO_2 extrusion in a shorter time (7, 5 h) than **2h** (10 h).

We verified that *N*-tosyl substituted 3,1-benzoxazin-2-one derivatives are more efficient aza-*ortho*-xylylene precursors than the corresponding *N*-tosyl substituted *o*-aminobenzyl alcohol **1c**. When compound **1c** and *N*-phenylmaleimide were heated in refluxing 1,2,4-trichlorobenzene H_2O was eliminated within 12 h to give intermediate **3c** which was trapped by the dienophile to afford **4c** (20%).

These results showed that *N*-tosyl substituted 3,1-benzoxazin-2-one derivatives can be used as aza-*ortho*-xylylene precursors under experimental conditions that enable them to undergo inter- and intra-molecular Diels–Alder reactions.

We continued studying the intermolecular cycloaddition reactions of aza-*ortho*-xylylenes with **2c** and a variety of dienophiles. Compound **2d** was less attractive from the synthetic point of view because of the competitive intramolecular 6π electrocyclization observed in the reaction with *N*-phenylmaleimide.

Thermolysis of **2c** in the presence of benzoylacetylene and (*E*)-1-benzoyl-2-phenylsulfonylethylene were completely regioselective in both cases giving 3-benzoylquinoline **7** in yields of 40 and 30%, respectively (Scheme 4).‡ The dihydro- and



Scheme 4 *Reagents and conditions:* i, 1,2,4-trichlorobenzene, reflux; ii, benzoylacetylene; iii, (*E*)-1-benzoyl-2-phenylsulfonylethylene; iv, (*E*)-1,2-dibenzoylethylene

tetrahydro-quinoline intermediates which arise by cycloaddition of **3c** with these dienophiles gained aromaticity by elimination of toluenesulfinic acid. Both these reactions could have led to a mixture of 2- and 3-benzoylquinolines. The isolation of **7** as the only regioisomer prompted us to check the stability of the other. A sample of 2-benzoylquinoline was unaffected upon being heated in refluxing 1,2,4-trichlorobenzene for 5 h and could be recovered quantitatively at the end of the reaction. The possibility that it might form and then decompose during the course of the reactions is ruled out.

Thermolysis of **2c** in the presence of (*E*)-1,2-dibenzoylethylene gave 2,3-dibenzoylquinoline **8** (15%) by toluenesulfinic acid elimination and oxidation of the tetrahydroquinoline derivative initially formed (Scheme 4).

The Diels–Alder reaction was somewhat limited and the reactions of **2c** with maleic anhydride, 1,4-benzoquinone, 1,4-naphthoquinone, dimethyl maleate, acrylonitrile, ethyl acrylate, β-nitrostyrene, β-nitroethylene, vinyl ether, dimethyl acetylenedicarboxylate, tosylacetylene and 1-phenyl-2-(phenylsulfonyl)-acetylene for instance, were unsuccessful giving only complex product mixtures. In some cases, when the dienophile (maleic anhydride, 1,4-naphthoquinone) was recovered at the end of the reaction, it was the result of the aza-*o*-xylylene intermediate **3c** being unstable. The non-recovery of the dienophile might

† An authentic sample of **6** was prepared independently (see Experimental section).

‡ The stability of (*E*)-1-benzoyl-2-phenylsulfonylethylene under the reaction conditions excludes its conversion into benzoylacetylene in the course of the reaction.

Table 1 Analytical and spectroscopic data of **2b–h**

Compd.	Bp (°C/mmHg) Mp (°C) (lit.) Solvent	Yield[a] (%)	ν_{max} (Nujol)/cm^{-1}	δ_H($CDCl_3$)	Found (%) (Required) C H N	*m/z* (EI) (M^+)
2b $C_9H_9NO_2$	130/0.1[b] (125–130/0.8[c])	70	1720	3.35 (3 H, s, NMe), 5.15 (2 H, s, CH_2O), 6.9–6.95 (1 H, m, ArH), 7.0–7.1 (2 H, m, ArH) and 7.4–7.5 (1 H, m, ArH)	66.2 5.5 8.5 (66.2 5.6 8.6)	163
2c $C_{15}H_{13}NO_4S$	153–154 AcOEt–hexane 9/1	60	1760	2.5 (3 H, s, Me), 5.1 (2 H, s, CH_2O), 7.2–7.3 (2 H, m, ArH), 7.35–7.4 (3 H, m, ArH), 7.55 (1 H, d *J* 8, ArH) and 8.15 (2 H, d, *J* 8, ArH)	59.4 4.5 4.7 (59.4 4.3 4.6)	303
2d $C_{21}H_{16}ClNO_4S$	116–117 Pr^i_2O	82	1750	2.4 (3 H, s, Me), 6.15 (1 H, s, CHO), 6.95 (1 H, br s, ArH), 7.2–7.5 (8 H, m, ArH), 7.6 (1 H, d *J* 8, ArH) and 7.8–7.85 (2 H, d, *J* 8, ArH)	61.0 3.8 3.4 (61.0 3.9 3.4)	413
2e $C_{21}H_{23}NO_4S$	72–73 AcOEt–pentane 9:1	83	1755 1630	1.4–1.65 (4 H, m, CH_2), 1.9–2.1 (4 H, m, CH_2), 2.48 (3 H, s, Me), 4.9–5.05 (2 H, m, CH_2=), 5.12 (1 H, t, *J* 7, CHO), 5.7–5.8 (1 H, m, CH=), 7.15–7.4 (5 H, m, ArH), 7.6 (1 H, d, *J* 8 ArH) and 8.15 (2 H, d, *J* 8, ArH)	65.25 5.9 3.7 (65.4 6.0 3.6)	385
2f $C_{12}H_{13}NO_4S$	110–111 AcOEt	48	1750 1640	2.7–2.8 (2 H, m, CH_2), 3.86–3.92 (2 H, m, CH_2), 5.14–5.24 (2 H, m, CH_2=), 5.19 (2 H, s, CH_2O), 5.79–5.93 (1 H, m, CH=) and 7.2–7.5 (4 H, m, ArH)	53.8 4.8 5.05 (53.9 4.9 5.2)	267
2g $C_{13}H_{15}NO_4S$	53–54 Pr^iOH–Pr^i_2O 9:1	75	1750 1630	2.1–2.2 (2 H, m, CH_2), 2.25–2.35 (2 H, m, CH_2), 3.79–3.84 (2 H, m, CH_2), 5.08–5.14 (2 H, m, CH_2=), 5.2 (2 H, s, CH_2O), 5.7–5.86 (1 H, m, CH=) and 7.3–7.5 (4 H, m, ArH)	55.4 5.5 4.85 (55.5 5.4 5.0)	281
2h $C_{11}H_{11}NO_4$	76–78 Pr^i_2O	55	1790 1710	1.4 (3 H, t, *J* 8, CH_2CH_3), 4.4 (2 H, q, *J* 8, CH_2CH_3), 5.2 (2 H, s, CH_2O), 7.2–7.55 (3 H, m, ArH) and 7.75 (1 H, d *J* 8, ArH)	59.6 5.1 6.15 (59.7 5.0 6.3)	221

[a] Relevant to pure isolated compounds. [b] Bulb-to-bulb distillation. [c] Ref. 17.

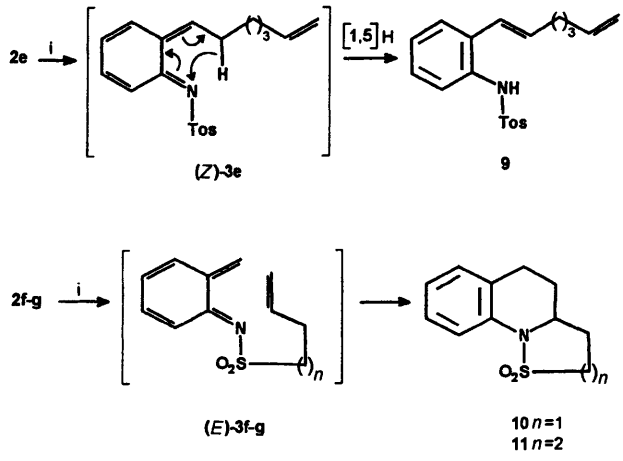
result from decomposition of the corresponding cycloadducts unstable at a high temperature (216 °C).

To study the intramolecular Diels–Alder reactions of aza-*ortho*-xylylenes generated from *N*-tosyl substituted 3,1-benzoxazin-2-ones, we used the 4-hex-5-enyl substituted derivative **2e** (Scheme 1).

Thermolysis of **2e** in refluxing 1,2,4-trichlorobenzene gave compound **9** (75%, 45 min) as the only product (Scheme 5). The formation of this is a result of a [1,5] hydrogen shift in the *Z*-isomer of the transient aza-*ortho*-xylylene **3e**. In contrast, 4-hex-5-enyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one on FVP (600 °C) undergoes intramolecular cycloaddition to give the octahydrophenanthridine derivative (30%).[3c] We found that at 216 °C the [1,5] hydrogen shift for the *Z*-isomer of **3e** was far faster than the intramolecular cycloaddition for the *E* isomer of **3e**. The latter reaction might be disadvantaged by the steric hindrance of the tosyl substituent.

The less hindered aza-*ortho*-xylylenes **3f,g**, unable to undergo a [1,5] hydrogen shift, underwent intramolecular cycloadditions. In fact, the *N*-but-3-enylsulfonyl and the *N*-pent-4-enylsulfonyl derivatives **2f,g**, when heated in boiling 1,2,4-trichlorobenzene, gave the expected tricyclic compounds **10** (24%) and **11** (34%) (Scheme 5) *via* the *E* isomers of **3f,g**; both reactions also afforded **2a** in yields of 29 and 22%, respectively. Formation of the latter may arise as a result of the N–S bond being ruptured upon thermolysis at 216 °C, as reported for *N*-arylbenzenesulfonamides heated at 300 °C.[9]

The introduction of an electron-withdrawing group such as a tosyl substituent into the corresponding 3,1-benzoxazin-2-one derivatives makes them attractive precursors of aza-*ortho*-xylylenes. The transient intermediates **3c,d**, generated under milder conditions than those reported, starting from *N*-alkyl, *N*-phenyl and *N*-alkylidene substituted 3,1-benzoxazin-2-ones,[3] undergo intramolecular and intermolecular Diels–Alder reactions with electron-deficient ethylenic and acetylenic dienophiles. These reactions, which lead to tetrahydroquinoline and quinoline derivatives in fairly good yields, are the first examples



Scheme 5 *Reagents and conditions:* i, 1,2,4-trichlorobenzene, reflux

of intermolecular cycloadditions involving aza-*ortho*-xylylenes generated from 3,1-benzoxazin-2-one derivatives.

It is worth comparing the reactivity of the azadienic intermediate **3c** with that of the linear *N*-phenylsulfonyl substituted 1-azabuta-1,3-dienes which are reported to have the strong character of 'inverse electron-demand' Diels–Alder dienes.[10] Probably the reactivity of **3c** with electron-poor dienophiles is the result of the electronic effects of the substituents bound to the nitrogen atom and C-2, C-3 carbon atoms of the azadienic system. A conjugating substituent on the C-2 carbon atom of the buta-1,3-diene enhances the HOMO energy level.[11] We could assume therefore, that in the azadienic intermediate **3c** the electron-deficient character imposed by the *N*-tosyl residue is reduced or balanced by the buta-1,3-dienylic substituent at C-2 and C-3. This would be consistent with the reactivity observed.

With non-symmetrical dienophiles, benzoylacetylene and (*E*)-1-benzoyl-2-phenylsulfonylethylene, the cycloaddition was completely regioselective. This regiochemistry is unusual and

difficult to explain on the basis of a qualitative frontier molecular orbital (FMO) analysis.

1-Substituted dienes react with electron-poor dienophiles giving the adduct with the dienophile substituent orientated '*ortho*' with respect to the diene substituent, independently of its electronic nature.[11] In general, the orientation is the same in the reactions of heterodienes with electron-poor dienophiles.[5,12,13] We should therefore expect the azadienic intermediate **3c** to react with benzoylacetylene giving the '*ortho*' adduct. However, we obtained only the adduct with the dienophile substituent in the β position with respect to the nitrogen substituent. In the case of (*E*)-1-benzoyl-2-phenylsulfonylethylene, as a dienophile, it is even harder to predict the preferred orientation, ignoring the structure of its FMOs.

However, our results are not the only ones in which an unusual regiochemical trend is observed when 1-azadienes are involved. Fowler has recently found that 2,4-substituted 1-azadienes displaying type II and type III Diels–Alder reactivity reacted with ethyl acrylate to give only the cycloadducts, with the carboxy group in the β position with respect to the nitrogen atom.[14] Probably some unpredictable factors such as multi-substitution of the azadienic system or secondary orbital interactions prevent a qualitative FMO analysis in the rationalization of the regiochemistry observed.

Experimental

Mps were measured with a Buchi apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer. All chemical shifts are expressed as δ values from tetramethylsilane as the reference; J values are expressed in Hz. The 2D NOESY[15] spectrum and the 1D reference spectrum were acquired using a Bruker DMX 500 spectrometer. $S/2$ t_1 increments were implemented over 2048 data points in the t_2 dimension: the mixing time was 800 ms and the spectra were collected in the phase-sensitive mode using the TPPI sequence. Mass spectra were determined on a VG Analytical 7070 EQ mass spectrometer with an attached VG Analytical 11/250 data system using EI and FAB techniques. *N*-Phenylmaleimide, 2-aminobenzyl alcohol **1a** and (*E*)-1,4-diphenylbut-2-ene-1,4-dione are commercial products. 2-Methylaminobenzyl alcohol **1b**,[16] 2-amino-5-chlorophenyl-(phenyl)methanol,[17] ethyl[2-(hydroxymethyl)phenyl]carbamic acid,[18] 1,4-dihydro-2*H*-3,1-benzoxazin-2-one **2a**,[17] *N*-(2-formylphenyl)-4-methylbenzenesulfonamide,[19] propiolophenone,[20] (*E*)-1-phenyl-3-phenylsulfonylprop-2-en-1-one[21] and 2-benzoylquinoline[22] were prepared according to reported procedures. Chloroform was distilled from phosphorus pentoxide. *N*,*N*-Dimethylformamide (DMF) and 1,3-dimethylimidazolidin-2-one (DMI) were kept at 80 °C for 8 h over CaH_2 and distilled at reduced pressure. After aqueous work-up of the reaction mixtures, organic solvents were dried with anhydrous sodium sulfate and evaporated on a rotatory evaporator under reduced pressure.

Table 2 Thermolysis of **2b–d,h** in the presence of *N*-phenylmaleimide

Entry	Substrate	Temperature (*T*/C°)	Time (t/h)	Cycloadduct	Yield (%)[a]
1	**2b**	216	15[b]	**4b**	17
2	**2c**	216	7	**4c**	47
3	**2d**	190	5	**4d**	16[c]
4	**2h**	216	10	**4h**	25

[a] After column chromatography. [b] The ^{1}H NMR analysis of the crude residue showed that it consisted of two components: **2b** and **4b** in the ratio of 2:1. [c] It just accounts for the yield of the cycloadduct **4d**.

General procedure for the preparation of 1c,d,f,g

A solution of **1a** (for the preparation of **1c**,**f**,**g**) or 2-amino-5-chlorophenyl(phenyl)methanol (for **1d**) (24.4 mmol) and pyridine (29.2 mmol) in dry $CHCl_3$ (90 cm^3) was treated dropwise with a solution of the appropriate sulfonyl chloride (27.0 mmol) in $CHCl_3$ (25 cm^3) at room temperature. The reaction mixture was stirred magnetically at room temperature for 2–3 h. However when pent-4-enylsulfonyl chloride or but-3-enylsulfonyl chloride§ was used, the addition conditions were different. The addition was made at −20 °C and the reaction mixtures affording **1f**, **1g** were magnetically stirred for 1 h at −20 °C and then overnight at room temperature. After evaporation of the reaction mixture to dryness the resulting residue was taken up in ethyl acetate (50 cm^3) and saturated aqueous ammonium chloride (40 cm^3). The organic phase was separated, dried and evaporated. The crude residues from the preparations of **1c** and **1d** were purified by crystallization. Those obtained from the preparations of **1f** and **1g** were purified by chromatography on silica gel with hexane–ethyl acetate (7:3) as eluent. A sample was further purified by crystallization.

***N*-(2-Hydroxymethylphenyl)-4-methylbenzenesulfonamide 1c.** Yield 88%, mp 146–148 °C (Pr^iOH) (lit.,[19] 148–150 °C).

***N*-{4-Chloro-2-[hydroxy(phenyl)methyl]phenyl}-4-methylbenzenesulfonamide 1d.** Yield 75%, mp 108–109 °C (from Pr^i_2O) (Found: C, 61.85; H, 4.8; N, 3.5. $C_{20}H_{18}ClNO_3S$ requires C, 61.9; H, 4.7; N, 3.6%); ν_{max}(Nujol)/cm^{-1} 3530 and 3260; δ_H($CDCl_3$) 2.40 (3 H, s, Me), 2.6 (1 H, br s, OH), 5.55 (1 H, br s, CH), 6.9–7.5 (12 H, m, ArH) and 7.85 (1 H, s, NH).

***N*-[2-(Hydroxymethyl)phenyl]but-3-ene-1-sulfonamide 1f.** Yield 16%, mp 53–54 °C (from Pr^i_2O–hexane, 9:1) (Found: C, 54.9; H, 6.2; N, 5.75. $C_{11}H_{15}NO_3S$ requires C, 54.8; H, 6.3; N,

§ To prepare the alkylidenesulfonyl chlorides required we used a reported method.[23] However, in our hands, the reactions failed to afford the expected products; in both cases the ^{1}H NMR spectra of the residues showed the absence of the olefinic pattern in the range of 4.9–6.3 ppm. However, we were able to prepare the compounds, albeit in low yields, by treating the corresponding sodium alkylidene sulfites with $POCl_3$ at RT for 6 h. The crude products were used without any further purification.

Table 3 Analytical and spectroscopic data for **4b–d,h**

Compd.	Mp(°C) Solvent	δ_H($CDCl_3$)	Found (%) (Required) C	H	N
4b	130–131	2.95 (1 H, dd *J* 14, 6.5, CH), 3.14 (1 H, dd, *J* 14, 3.5, CH), 3.2 (3 H, s, NMe), 3.6–3.7	73.9	5.6	9.5
$C_{18}H_{16}N_2O_2$	Pr^iOH	(1 H, m, CH), 4.2 (1 H, d, *J* 9.5, CH), 6.8–7.5 (9 H, m, ArH)	(73.95	5.5	9.6)
4c	223–224	2.25 (1 H, dd *J* 15, 8, CH), 2.45 (3 H, s, Me), 2.96 (1 H, dd, *J* 15, 1, CH), 3.6–3.7	66.7	4.85	6.5
$C_{24}H_{20}N_2O_4S$	EtOH	(1 H, m, CH), 5.6 (1 H, d, *J* 9.5, CH), 6.8–6.85 (2 H, m, ArH), 7.05–7.35 (9 H, m, ArH) and 7.7 (2 H, d, *J* 8, ArH)	(66.65	4.7	6.5)
4d	250–252	2.5 (3 H, s, Me), 3.5 (1 H, d, *J* 6.5, CH), 3.8 (1 H, dd, *J* 9, 6.5, CH), 5.7 (1 H, d, *J* 9, CH),	66.3	4.25	5.1
$C_{30}H_{23}ClN_2O_4S$	AcOEt	6.9–7.4 (15 H, m, ArH) and 7.75 (2 H, d, *J* 8, ArH)	(66.35	4.3	5.2)
4h	138–139	1.2–1.4 (3 H, br m, CH_2CH_3), 2.95 (1 H, dd, *J* 14.5, 7, CH), 3.2 (1 H, dd *J* 14.5, 1, CH),	68.45	5.15	8.0
$C_{20}H_{18}N_2O_4$	Pr^iOH–Pr^i_2O 9:1	3.7–3.8 (1 H, m, CH), 4.15–4.4 (2 H, br m, CH_2CH_3), 5.7–5.9 (1 H, br m, CH), 6.8–6.9 (2 H, m, ArH) and 7.1–7.4 (7 H, m, ArH)	(68.6	5.2	8.0)

5.8%); ν_{max}(Nujol/cm^{-1}) 3445 and 1640; δ_H($CDCl_3$) 2.3 (1 H, br s, OH), 2.55–2.6 (2 H, m, CH_2), 3.19–3.24 (2 H, m, CH_2), 4.77 (2 H, s, CH_2), 5.06 (1 H, br d, *J* 10, CH=), 5.1 (1 H, dd, *J* 17, 1.5, CH=), 5.7–5.84 (1 H, m, CH=), 7.1–7.4 (3 H, m, ArH), 7.55 (1 H, d, *J* 8, ArH) and 7.8 (1 H, s, NH).

***N*-[2-(Hydroxymethyl)phenyl]pent-4-ene-1-sulfonamide 1g.**
Yield 30%, mp 50–51 °C (from Pr^i_2O–hexane, 9:1) (Found: C, 56.45; H, 6.7; N, 5.45. $C_{12}H_{17}NO_3S$ requires C, 56.5; H, 6.7; N, 5.5%); ν_{max}(Nujol)/cm^{-1} 3450 and 1640; δ_H($CDCl_3$), 1.93 (2 H, quintet, *J* 7, CH_2), 2.1 (2 H, quartet, *J* 7, CH_2), 2.3 (1 H, t, *J* 5, OH), 3.1–3.16 (2 H, m, CH_2), 4.8 (2 H, d, *J* 5, CH_2), 4.9–5.0 (2 H, m, CH_2=), 5.6–5.76 (1 H, m, CH=), 7.1–7.35 (3 H, m, ArH), 7.5 (1 H, d *J* 8, ArH) and 7.8 (1 H, br s, NH).

Preparation of *N*-[2-(1-hydroxyhept-6-enyl)phenyl]-4-methylbenzenesulfonamide 1e
To magnesium turnings (0.1 g, 4.3 mmol) suspended in dry THF (4 cm^3), a solution of 6-bromohex-1-ene (0.74 g, 4.6 mmol) in dry THF (3 cm^3) was added at a rate such as to maintain the temperature of the reaction mixture at 45–50 °C. After the addition, the reaction mixture was set aside at 50 °C for 30 min and then cooled to 0 °C and treated with a solution of *N*-(2-formylphenyl)-4-methylbenzenesulfonamide in dry THF (10 cm^3). After 30 min at 0 °C the reaction mixture was concentrated and the residue taken up in dichloromethane (CH_2Cl_2) (15 cm^3) and treated with saturated aqueous ammonium chloride (10 cm^3). The organic phase was separated, dried and evaporated. Recrystallization of the crude residue afforded **1e** as a solid (90%), mp 67–68 °C (Pr^i_2O–hexane, 9:1) (Found: C, 66.7; H, 7.0; N, 3.8. $C_{20}H_{25}NO_3S$ requires C, 66.8; H, 7.0; N, 3.9%); ν_{max}(Nujol)/cm^{-1} 3480, 3200 and 1640; δ_H($CDCl_3$) 0.95–1.65 (6 H, m, CH_2), 1.95 (2 H, quartet, *J* 7, CH_2), 2.3 (1 H, br s, OH), 2.38 (3 H, s, Me), 4.5–4.65 (1 H, m, CH), 4.9–5.02 (2 H, m, CH_2=), 5.67–5.8 (1 H, m, CH=), 6.95–7.7 (8 H, m, ArH) and 8.4 (1 H, br s, NH).

General procedure for the preparation of 3,1-benzoxazin-2-ones 2b–g ¶
To the appropriate *o*-aminobenzyl alcohol **1b–g** (14 mmol) in dry THF (150 cm^3), kept at −70 °C with magnetic stirring and a nitrogen atmosphere a BuLi solution (1.63 M in hexane; 19 cm^3, 31 mmol) was added dropwise. The reaction mixture was left at −70 °C for 15–30 min after which a phosgene solution (1.93 M in toluene; 8.3 cm^3, 16 mmol) diluted with dry THF (70 cm^3) was added. After the addition, the reaction mixture was allowed to react at room temperature for 2–3 h. It was then concentrated and the residue taken up in CH_2Cl_2 (60 cm^3) and the solution washed with saturated aqueous ammonium chloride (30 cm^3). The organic phase was separated, dried and evaporated. The crude residue was purified by bulb-to-bulb distillation in the case of *N*-methyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one **2b**; by chromatography (silica gel, toluene–ethyl acetate 9:1 as eluent) and crystallization in the case of N-(4-*methylphenylsulfonyl*)-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2c**, 6-*chloro*-N-(4-*methylphenylsulfonyl*)-4-*phenyl*-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2d**, 4-*hex*-5-*enyl*-N-(4-*methylphenylsulfonyl*)-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2e**, N-*but*-3-*enyl*-*sulfonyl*-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2f** and N-*pent*-4-*enyl*-*sulfonyl*-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2g** (Table 1).

¶ The reaction with ethyl [2-(hydroxymethyl)phenyl]carbamate gave a mixture which upon isolation furnished two products: the first product was bis[{2-[(ethoxycarbonyl)amino]phenylmethyl}] carbonate (51%), mp 160–161 °C (Pr^i_2O–Pr^iOH, 9:1) (Found: C, 60.45; H, 5.7, N, 6.7. $C_{21}H_{24}N_2O_7$ requires C, 60.6; H, 5.8; N, 6.7%); ν_{max}(Nujol/cm^{-1}) 3250, 1760 and 1680; δ_H(DMSO) 1.2 (6 H, t, *J* 8, CH_2CH_3), 4.1 (4 H, q, *J* 8, CH_2CH_3), 5.2 (4 H, s, CH_2), 7.1–7.45 (8 H, m, ArH) and 9.05 (2 H, s, NH); *m*/*z* (EI) 416 (M^+, 14%) and 178 (100); and the second was **2a** (13%), mp 118–119 °C (CH_2Cl_2–hexane, 1:1) (lit.,[17] 119–120 °C).

Procedure for the preparation of 2h
A suspension of sodium hydride (0.48 g, 20.0 mmol) in dry DMI (7 cm^3), kept at 0 °C under nitrogen atmosphere and with magnetic stirring was treated with a solution of **2a** (3.0 g, 20.0 mmol) in DMI (25 cm^3). After the hydrogen evolution had ceased, freshly distilled ethyl chloroformate (2.62 g, 24.2 mmol) in DMI (8 cm^3) was added dropwise to the reaction mixture. It was then allowed to react at 0 °C for 2 h after which it was brought to pH 5–6 with acetic acid and the solvent removed by distillation under reduced pressure (bp 40 °C, 0.2 mmHg). The residue was taken up in CH_2Cl_2 (25 cm^3) and water (10 cm^3) and the organic phase was separated, dried and evaporated to dryness. The solid residue purified by chromatography (silica gel with hexane–ethyl acetate, 7:3 as eluent) and crystallization gave N-*ethoxycarbonyl*-1,4-*dihydro*-2H-3,1-*benzoxazin*-2-*one* **2h** (Table 1).

General procedure for the thermolysis of 2b–d,h in the presence of *N*-phenylmaleimide
A mixture of the corresponding benzoxazin-2-one derivative (1.3 mmol) and *N*-phenylmaleimide (0.27 g, 1.56 mmol) was heated in refluxing 1,2,4-trichlorobenzene (8 cm^3) until the starting material disappeared (Table 2) (TLC: silica gel, toluene–ethyl acetate, 9:1). The solvent was removed by distillation under reduced pressure (80 °C, 0.4 mmHg) and the residue was taken up in CH_2Cl_2 (15 cm^3). The solution was washed with 5% aqueous sodium hydrogen carbonate (10 cm^3) and brine (8 cm^3), dried and evaporated. Each crude residue was purified by chromatography (silica gel, toluene–ethyl acetate, 9:1 as eluent) and crystallization. The reactions of **2b**,**c**,**h** with *N*-phenylmaleimide led to 4-*methyl*-2-*phenyl*-2,3,3a,4,9,9a-*hexahydro*-1*H*-*pyrrolo*[3,4-b]*quinoline*-1,3-*dione* **4b**, 4-(4-*methylphenylsulfonyl*)-2-*phenyl*-2,3,3a,4,9,9a-*hexahydro*-1*H*-*pyrrolo*[3,4-b]*quinoline*-1,3-*dione* **4c**, 4-*ethoxycarbonyl*-2-*phenyl*-2,3,3a,4,9,9a-*hexahydro*-1*H*-*pyrrolo*[3,4-b]-*quinoline*-1,3-*dione* **4h**, respectively (Tables 2 and 3). Thermolysis of **2d** in the presence of *N*-phenylmaleimide gave a mixture of three components, which were separated by chromatography on silica gel (hexane–ethyl ether, 4:6) and crystallized. The products isolated were in order of elution: 2-chloroacridine **5**: (12%), mp 172–173 °C (AcOEt) (lit.,[24] 170 °C) (Found: C, 73.0; H, 3.7; N, 6.5. Calc. for $C_{13}H_8ClN$: C, 73.1; H, 3.8; N 6.6%); δ_H($CDCl_3$) 7.6 (1 H, m, ArH), 7.7 (1 H, m, ArH), 7.3 (1 H, m, ArH), 8.0 (2 H, m, ArH), 8.2 (2 H, m, ArH) and 8.7 (1 H, s, ArH); *m*/*z* (EI) 213 (M^+, 100%); (3a*R**,9*S**,9a*S**)-7-*chloro*-2,9-*diphenyl*-4-(4-*methylphenylsulfonyl*)-2,3,3a,4,9,9a-hexahydro-1H-*pyrrolo*[3,4-b]*quinoline*-1,3-*dione* (**4d**) (Tables 2 and 3); N-{4-*chloro*-2-[*phenyl*(4-*methylphenylsulfonyl*)-*methyl*]*phenyl*}-4-*methylbenzenesulfonamide* **6** (3%); mp 197–198 °C (from ethyl acetate–hexane, 9:1) (Found: C, 61.8; H, 4.7; N, 2.85. $C_{27}H_{24}ClNO_4S_2$ requires C, 61.65; H, 4.6; N, 2.7%); ν_{max}(Nujol)/cm^{-1} 3300; δ_H($CDCl_3$), 2.35 (3 H, s, Me), 2.45 (3 H, s, Me), 5.68 (1 H, s, CH) and 7.05–7.7 (17 H, m, ArH and NH).

Thermolysis of 2d
Compound **2d** (0.8 g, 1.9 mmol) was heated at 220 °C/16 mmHg in a sublimation apparatus until the starting material disappeared (TLC on silica gel, toluene–ethyl acetate, 9:1). A yellow solid condensed on the tip of the cooling finger whose analytical and spectroscopic properties were identical with those of **5**; yield 20%. The residue, chromatographed on silica gel with toluene–ethyl acetate, 9:1, gave **6** (0.16 g, 16%).

Independent synthesis of 6
To a solution of **1d** (0.19 g, 0.5 mmol) and triethylamine (0.06 g, 0.6 mmol) in toluene (10 cm^3), kept at 0 °C and magnetically stirred, a solution of methanesulfonyl chloride (0.07 g, 0.6 mmol) in toluene (2 cm^3) was added dropwise. The mixture was left 1 h at 0 °C after which it was filtered and the filtrate

was diluted with diethyl ether (20 cm^3). The organic phase was washed with water (10 cm^3), dried and evaporated to afford the crude methanesulfonate. This, used without any further purification, was dissolved in dry DMF (7 cm^3) and treated with sodium benzenesulfinate (0.18 g, 1 mmol) in dry DMF (3 cm^3). The reaction mixture was refluxed for 4 h after which it was evaporated and the residue suspended in water (15 cm^3). The suspension was brought to pH 5 with acetic acid and then extracted with CH_2Cl_2 (2 × 15 cm^3). The combined extracts were dried and evaporated and the crude residue chromatographed (silica gel, diethyl ether–hexane, 6:4 as eluent) to give a product whose analytical and spectroscopic data were coincident with those of **6** (0.1 g, 40%).

Thermolysis of 2c in the presence of benzoylacetylene

A glass liner containing **2c** (0.4 g, 1.32 mmol) and the dienophile (0.21 g, 1.58 mmol), in 1,2,4-trichlorobenzene (8 cm^3) was placed inside a stainless-steel autoclave. The air in the autoclave was replaced by N_2 (60 atm). The autoclave was heated at 250 °C by means an external silicon oil bath for 6 h. The autoclave was cooled and the reaction mixture was worked-up and purified as described in the general procedure giving 3-benzoylquinoline **7** (40%), bp 150 °C/0.1 mmHg, mp 75–77 °C (lit.,[25] 76–77 °C) (Found: C, 82.5; H, 4.8; N, 5.85. Calc. for $C_{16}H_{11}NO$: C, 82.4; H, 4.75; N, 6.0%); $\delta_H(CDCl_3)$ 7.45–7.9 (8 H, m, ArH), 8.2 (1 H, m, ArH), 8.55 (1 H, s, ArH) and 9.35 (1 H, s, ArH).

Thermolysis of 2c in the presence of (*E*)-1-benzoyl-2-phenylsulfonylethylene or (*E*)-1,2-dibenzoylethylene

A mixture of **2c** (0.4 g, 1.3 mmol) and the ethylenic dienophile (1.56 mmol) in 1,2,4-trichlorobenzene (5 cm^3) was refluxed for 6–7 h. In both cases the reaction mixtures were subjected to work-up and purification as described in the general procedure. The thermolysis of **2c** with (*E*)-1-benzoyl-2-phenylsulfonylethylene gave **7** (30%). The thermolysis of **2c** in the presence of (*E*)-1,2-dibenzoylethylene gave 2,3-dibenzoylquinoline **8** (15%), mp 174 °C (from Pr^iOH) (lit.,[26] 172–173 °C); $\delta_H(CDCl_3)$ 7.4–7.95 (11 H, m, ArH), 8.1 (2 H, d, *J* 8, ArH), 8.2 (1 H, d, *J* 8, ArH) and 8.4 (1 H, s, ArH); *m/z* (EI) 337 (M^+, 45%) and 105 (100).

General procedure for the thermolysis of benzoxazin-2-ones 2e–g

Each of the benzoxazin-2-ones **2e–g** (1.7 mmol) was refluxed in 1,2,4-trichlorobenzene (20 cm^3) until the starting material disappeared (45 min for **2e**, 120 min for **2f,g**). The solvent was removed by distillation and the residue was taken up in CH_2Cl_2 (15 cm^3). The solution was washed with 5% aqueous sodium hydrogen carbonate (8 cm^3), dried and evaporated. The crude residue was chromatographed on silica gel with hexane–ethyl acetate (7:3) as eluent. The thermolysis of **2e** gave N-[2-(1*E*)-*hepta*-1,6-*dienylphenyl*]-4-*methylbenzenesulfonamide* **9** (75%), mp 75–77 °C (from hexane) (Found: C, 70.3; H, 6.7; N, 3.95. $C_{20}H_{23}NO_2S$ requires C, 70.35; H, 6.8; N, 4.1); ν_{max}(Nujol/cm^{-1}) 3260 and 1640; δ_H(DMSO) 1.4 (2 H, quintet, *J* 7.5, CH_2), 2.0–2.1 (4 H, m, CH_2), 2.4 (3 H, s, Me), 5.0–5.05 (2 H, m, CH_2=), 5.7–5.8 (1 H, m, CH=), 6.03 (1 H, dt, *J* 15.5, 7, CH=), 6.4 (1 H, d, *J* 15.5, CH=), 6.9–7.5 (8 H, m, ArH) and 9.6 (1 H, br s, NH); *m/z* (EI) 341 (M^+, 30%) and 187 (100).

The thermolysis of **2f** gave 3,3a,4,5-*tetrahydroisothiazolo*-[2,3-a]*quinoline* 1,1-*dioxide* **10** (24%), mp 164–165 °C (from Pr^iOH) (Found: C, 59.35; H, 6.05; N, 6.4. $C_{11}H_{13}NO_2S$ requires C, 59.2; H, 5.9; N, 6.3%); $\delta_H(CDCl_3)$ 1.77–1.90 (1 H, m, CH), 2.05–2.28 (2 H, m, CH), 2.53–2.63 (1 H, m, CH), 2.8–2.95 (2 H, m, CH), 3.36 (2 H, dd, *J* 9, 6, CH_2), 3.82–3.92 (1 H, m, CH), 6.9–7.2 (3 H, m, ArH) and 7.6 (1 H, d, *J* 8, ArH); *m/z* (EI) 223 (M^+, 90%) and **131** (100); **2a** (29%), mp 118–119 °C (CH_2Cl_2–hexane, 1:1) (lit.,[17] 119–120 °C). The thermolysis of **2g** gave 2,3,4,4a,5,6-*hexahydrothiazino*[2,3-a]-*quinoline* 1,1-*dioxide* **11** (34%), mp 90–91 °C (Pr^iOH–Pr^i_2O, 9:1) (Found: C, 60.8; H, 6.35; N, 6.05. $C_{12}H_{15}NO_2S$ requires C, 60.75; H, 6.4; N, 5.9%); $\delta_H(CDCl_3)$ 1.48–1.85 (3 H, m, CH), 2.13–2.24 (2 H, m, CH), 2.28–2.45 (1 H, m, CH), 2.65–2.72 (2 H, m, CH), 3.07–3.12 (1 H, ddd, *J* 12.5, 13, 4, CH), 3.2–3.3 (1 H, tt, *J* 13, 4, CH), 4.25–4.35 (1 H, m, CH), 6.8–8.0 (3 H, m, ArH) and 7.6–7.7 (1 H, d, *J* 8, ArH); *m/z* (FAB) 237 (M^+); **2a** (22%).

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