The 'inverse electron-demand' Diels–Alder reaction in polymer synthesis. Part 2.[1] Some bis(1,2,4-triazines) as potential bis-diene monomers †

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Synthetic approaches to a series of 5,5′-linked bis(1,2,4-triazines) are described: these are potential monomers in Diels–Alder polymerisation processes.

Oxidation of bis(α-bromophenylacetyl) substituted aromatic compounds with dimethyl sulfoxide, or (better) oxidation of diacetyl- or bis-(phenylacetyl) substituted aromatic compounds with hydrogen bromide in dimethyl sulfoxide, gives the corresponding bis(1,2-diketones) and bis(α-keto aldehydes); these are converted into 3,3′-bis(methylsulfanyl)-5,5′-arylenebis(1,2,4-triazines) by reaction with *S*-methylthiosemicarbazide. The methylsulfanyl groups may then be oxidised by standard methods to give the corresponding methylsulfinyl or methylsulfonyl compounds, although the oxidised products show a tendency to decompose on storage.

Polymers with an 'all-aromatic' (or heteroaromatic) backbone continue to be of interest for a variety of 'high-performance' applications. The synthesis of such polymers is usually achieved by functional group transformations (*e.g.* electrophilic or nucleophilic aromatic substitution) on monomers containing pre-formed aromatic or heteroaromatic rings; an alternative approach, however, involves the formation of an aromatic or heteroaromatic ring in the polymerisation step. This latter approach has been largely neglected, partly because simple benzene derivatives are available in such wide variety, and partly because methods for the synthesis of benzene rings have not been widely developed. The comparative neglect in the heteroaromatic area, however, is perhaps surprising, given the range and diversity of methods available for the synthesis of heteroaromatic ring systems.

The Diels–Alder reaction has been used extensively for preparing polyimides;[2–4] otherwise, however, there are few examples of its application in aromatic or heteroaromatic polymer synthesis. This may be due, in part, to the reversible nature of the Diels–Alder reaction, which means that polymers formed by such processes are likely to have limited thermal stability. If, however, the initial cycloadduct can lose a small volatile molecule (*e.g.* carbon monoxide or dioxide, nitrogen, or ethene) and is thereby converted irreversibly into a (thermally stable) aromatic or heteroaromatic moiety, a potentially useful polymer-forming process may result. The best-known process of this type is based on the reactions of alkynes with tetraphenylcyclopentadienone ('tetracyclone')[5] or α-pyrones,[6] which give simple substituted benzenes along with carbon monoxide or dioxide respectively; extensions of these reactions, using bis-tetracyclones and bis(alkynes)[7] or bis(α-pyrones) with either bis(alkynes)[8] or bis(maleimides)[9] have been used for the formation of polymers (Scheme 1).

Diels–Alder reactions in simple heterocyclic ring systems have probably been most widely investigated in 1,2,4-triazines. Both 'normal' and 'inverse electron-demand' types have been observed, although the latter constitute the vast majority.[10] Cycloaddition usually occurs across C-3 and C-6, or (occasionally) across N-2 and C-5. The former is almost invariably followed by spontaneous loss of molecular nitrogen (Scheme 2): the use of an alkyne as dienophile in these Diels–Alder reactions thus leads directly to pyridines, whereas alkenic dienophiles give 3,4-dihydropyridines as the primary products. Our current efforts are directed towards the application of such inverse electron-demand Diels–Alder reactions to the synthesis of polymers.

In Part 1,[1] we have described the syntheses of a range of bis(alkynes) which are potential bis(dienophiles) in polymerisations. Bis(1,2,4-triazines) are, therefore, attractive synthetic targets for potential use as bis(dienes). Relatively little is known about such compounds, although sporadic reports of the synthesis of 3,3′- and 5,5′-linked systems have appeared in the literature. The latter type is the more attractive for our purposes, both for steric reasons (a Diels–Alder reaction across C-3 and C-6 might be expected to be less subject to hindrance in the 5,5′-linked series) and because the expected polymer end-product might contain at least a proportion of (linear) 2,5-disubstituted pyridine units.

It is known that oxidative coupling of 3-methylsulfanyl-1,2,4-triazine, **1**, to give the 5,5′-linked bis(triazine) **2**, is brought about by the action of potassium cyanide[11,12] or sodium in dry methanol (Scheme 3);[11] a high yield in the former reaction, however, requires a considerable excess (5 mol equiv.) of potassium cyanide, and in the reaction involving sodium, nucleophilic substitution of the methylsulfanyl group by methoxide (giving **3** and/or **4**) can be a complicating factor. It has also been claimed that 3-methyl- and 3-*p*-tolyl-1,2,4-triazines are coupled photochemically through C-5 and C-5′, although the experimental procedure does not appear to have been published.[13]

1,2,4-Triazines are most easily prepared by reaction of 1,2-dicarbonyl compounds with semicarbazide derivatives. Semicarbazide itself tends to give only acyclic semicarbazones which require to be cyclised in a separate step,[14] but reactions involving *S*-methylthiosemicarbazide‡ give the 3-methylsulfanyltriazine directly.[15] Hydrazidines and amidrazones may be used in place of semicarbazide derivatives;[16] the reactions of

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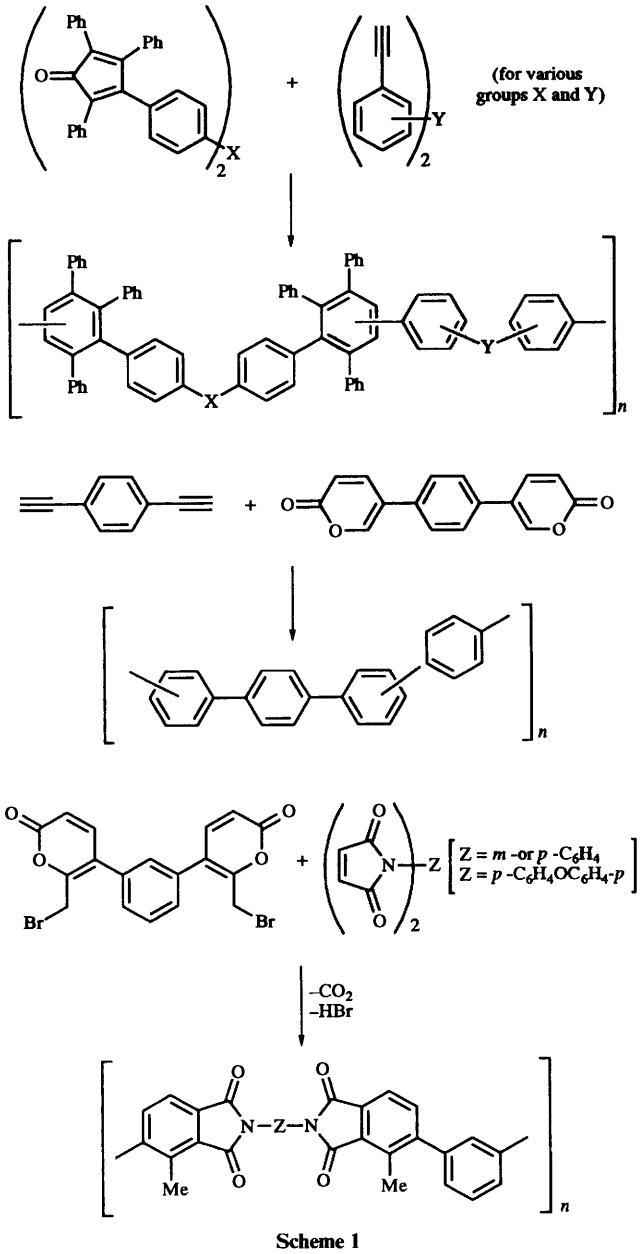
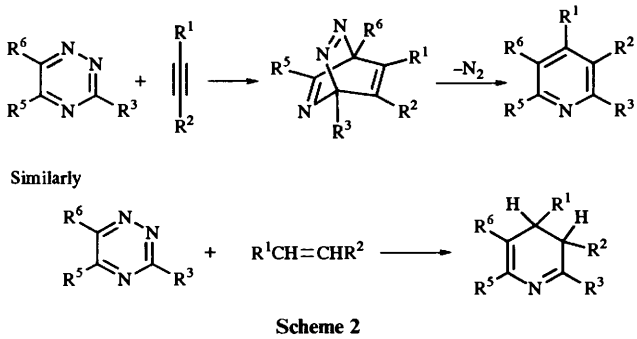
‡ This name, retained for convenience, refers to the compounds $H_2NC(SMe)=NNH_2$; such compounds are correctly named as *S*-methyl thiocarbamide hydrazones.



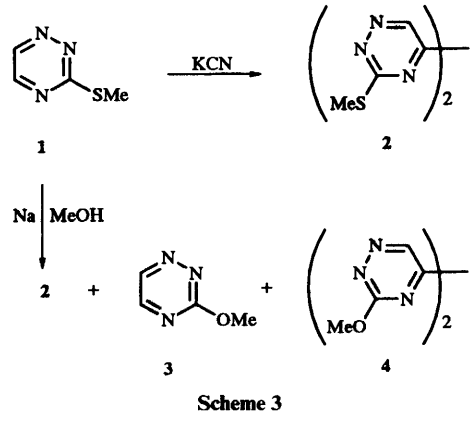
Scheme 1



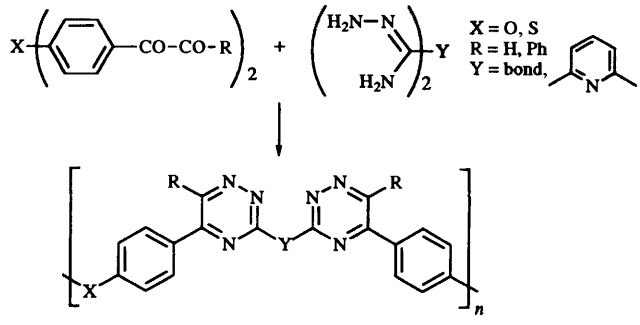
Scheme 2

amidrazones with bis(1,2-dicarbonyl) compounds[17] constitute what is, perhaps, the only potentially *general* synthesis of 5,5′-linked bis(1,2,4-triazines) described to date, and the reactions of bis(amidrazones) and bis(1,2-dicarbonyl) compounds are known to give poly(arylene-1,2,4-triazines)[18,19] (Scheme 4).

Our investigation has been concerned with two routes to 5,5′-linked bis(1,2,4-triazines), *viz.* reactions of bis(1,2-dicarbonyl) compounds with *S*-methylthiosemicarbazide, and coupling of two suitably functionalised 1,2,4-triazines to a central 'core'. This paper deals with the first of these. The choice of *S*-methylthiosemicarbazide as the cyclising agent has the additional advantage that the 3-methylsulfanyl substituent in the resulting triazine may be oxidised to methylsulfinyl or methylsulfonyl, thereby enhancing the electron-deficient character of the triazine ring and promoting inverse electron-demand Diels–Alder cycloadditions.[20]



Scheme 3

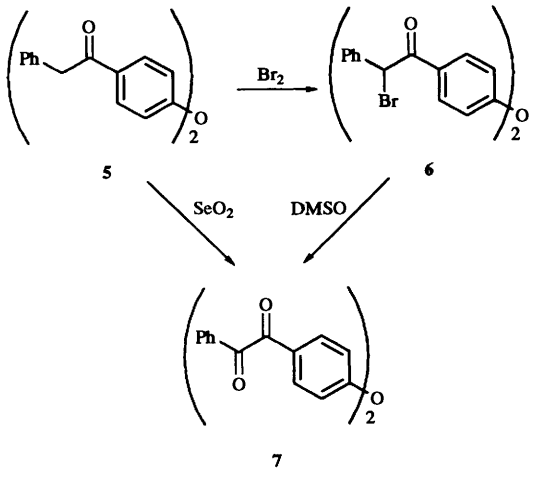


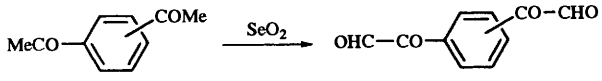
Scheme 4

Synthesis of bis(1,2-dicarbonyl) compounds

The classical method for the synthesis of an unsymmetrically substituted 1,2-dicarbonyl compound involves oxidation of the corresponding CH_2CO compound using selenium dioxide.[21] This has been used with some success for the production of bis(1,2-diketones) such as *p,p′*-oxydibenzil, **7**,[22,23] and bis(keto aldehydes) such as *p*- and *m*-phenylenebis(glyoxals), **8a**[24] and **8b**[25] (Scheme 5). For other than small-scale syntheses, however (*i.e.* where column chromatography is not practicable), the use of selenium dioxide is unsatisfactory. Not only are selenium compounds toxic, but the elemental selenium which is obtained as the co-product tends to precipitate *very* slowly (over a period of days) from the reaction mixtures, thus making its complete removal a troublesome problem. We have therefore sought alternative methods for effecting this oxidation which are applicable both to oxidation at *two* sites in the starting compound and, in principle at least, to large-scale processes.

Conversion of methylene ketones into 1,2-diketones or α-keto aldehydes may also be brought about by bromination of the methylene group and oxidation of the resulting α-bromo ketone with dimethyl sulfoxide;[26] an extension of this method to the synthesis of arylenebis(glyoxals) has also been reported in the literature.[27] In our hands, however, although the method is successful for the oxidation of bis[*p*-(2-bromo-2-phenylacetyl)-phenyl] ether, **6**, to the corresponding bis(benzil) **7** (Scheme 5), it has failed to oxidise the bis(bromoacetyl) compounds **9**, **10a**



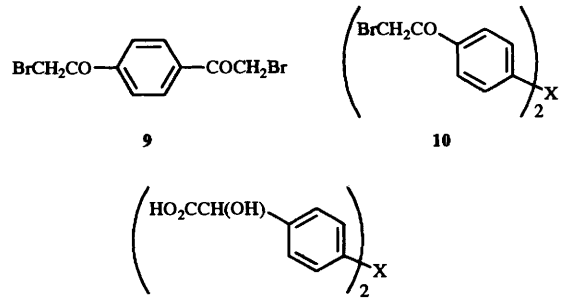


8a *p*-C_6H_4; b *m*-C_6H_4

Scheme 5

and **10e** cleanly to the bis(glyoxals) **8a**, **14a** and **14e**: in each case substantial amounts of unreacted dibromo-compound are recovered. Attempted oxidations of **9**, **10a**, and **10e** to **8a**, **14a** and **14e** using pyridine *N*-oxide[28] or trimethylamine *N*-oxide[29] result in the production of very high-melting materials which remain unidentified. It is possible that these unwanted products result from over-oxidation, or from a condensation of the bis(glyoxals) with the starting compounds. It is also known[30] that α-keto aldehydes may be susceptible to undergo a benzil-benzilic acid type of rearrangement in presence of base, and it is therefore possible that the high-melting materials (which show an NMR signal at *ca.* δ_H 12) may be bis(mandelic acids), *e.g.* **11**.

A 'one-pot' alternative to the above bromination–oxidation sequence involves the use as oxidant of dimethyl sulfoxide (in some cases with added hydrogen peroxide) and concentrated hydrobromic acid. Stilbenes are thereby oxidised to benzils,[31] and acetophenones to phenylglyoxals.[32] Oxidation of *p*-



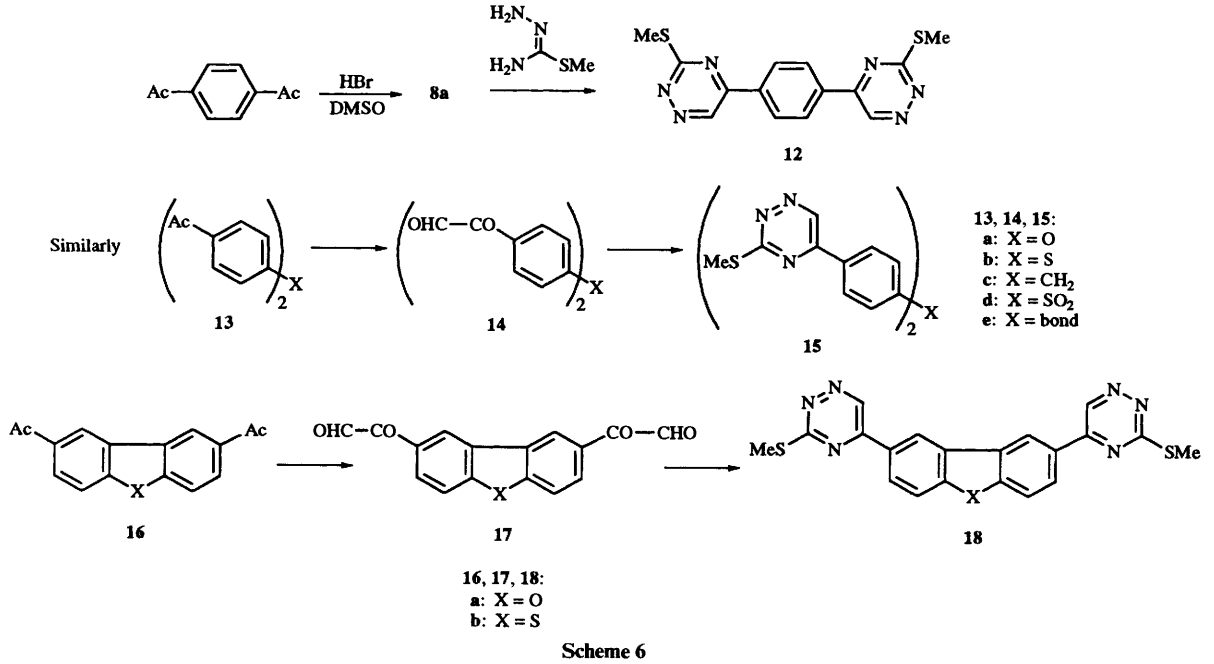
11

a: X = O; e: X = bond

diacetylbenzene and the diacetyl compounds **13a–e** and **16a–b** by this method (in the absence of added peroxide) leads to the bis(glyoxals) **8a**, **14a–e** and **17a–b** (Scheme 6) in moderate to high yield (Table 1), and is now our preferred synthetic route to such compounds. The bis(glyoxals) are obtained as hydrates, as shown by their ^{1}H NMR spectra, in which the hydrated 'formyl' protons [R-C*H*(OH)$_2$] resonate in the range δ_H 5.5–6. The previously recorded melting points of some of these compounds show wide variation: the discrepancies probably result from the gradual dehydration which occurs on heating. The crude bis(glyoxals) are generally of sufficient purity that they can be used directly, although (with the exception of **17b**) they can be recrystallised if necessary from aqueous dioxane. The corresponding oxidation of bis-*p*-(phenylacetyl)phenyl ether, **5**, gives *p*,*p*′-oxydibenzil, **7**, in acceptable yield.

Synthesis of bis(1,2,4-triazines)

Reaction of the hydrated bis(glyoxals) at room temperature with *S*-methylthiosemicarbazide, generated *in situ* from the corresponding hydriodide salt using sodium hydrogen carbonate, gives the corresponding bis(3-methylsulfanyl-1,2,4-triazines) **12**, **15a–e** and **18a** (Scheme 6) in acceptable yields (Table 2). The yields are not significantly improved by the use of purified bis(glyoxals). The characteristic resonances of the triazine ring protons (6-H) are observed in each case at δ_H *ca.* 9.4, and those of the C-3 carbons at δ_C 173.5–174.5. Attempts to prepare the dibenzothiophene-containing analogue **18b** have

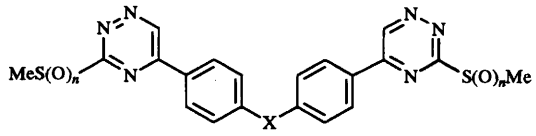


Scheme 6

not proved entirely successful: although the product appears pure by NMR, it has not been obtained in analytical purity, and the nature and source of the impurity are as yet unknown.

Oxidation of the methylsulfanyl substituents

Oxidation of methylsulfanyl groups to their methylsulfonyl counterparts has most commonly been effected for mono-1,2,4-triazines using *m*-chloroperbenzoic acid.[33] Complete oxidation of the two representative bis(3-methylsulfanyl-1,2,4-triazines) **15a** and **15e** does not, however, occur under these conditions, the use of an excess of oxidant leading only to mixtures of sulfoxides and sulfones (sulfoxide:sulfone = *ca.* 1:3). The bis(3-methylsulfinyl-1,2,4-triazines) **19a** and **19e** are, however,



19 $n = 1$
20 $n = 2$

19a, 20a: X = O; **19e, 20e**: X = bond

obtained cleanly and in good yield by oxidation using 2 mol equiv. of *m*-chloroperbenzoic acid. The best route to the bis(3-methylsulfonyl-1,2,4-triazines) **20a** and **20e** uses an adaptation of a published procedure for oxidation of alkyl phenyl sulfides,[34] the oxidant being oxone® in the presence of moist alumina; under these conditions no contamination by partially oxidised products is observed. The bis(sulfoxides) and the bis(sulfones) are all unstable, both thermally and on storage; they appear to be sensitive to both air and moisture. In all cases, therefore, these compounds are best prepared immediately prior to use in further transformations.

The potential utility of these bis(triazines) in polymerisation processes is currently being assessed by means of a series of model reactions with monofunctional electron-rich dienophiles. A similar assessment of the diethynyl compounds described in Part 1[1] is being carried out using simple azadienes. Whereas, regrettably, intermolecular Diels–Alder reactions do not apparently occur between the bis(triazines) and simple arylalkynes, or between the diethynyl compounds and simple 1,2,4-triazines, suitable reaction 'partners' for both series have been identified, and these will be reported in Part 3 (currently in preparation); the syntheses of the required difunctional analogues are now also in progress.

Experimental

Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected; IR spectra, recorded on a Perkin-Elmer 1710 FT spectrometer, are those of Nujol mulls. ^{1}H NMR spectra were obtained at either 200 or 300 MHz and ^{13}C spectra at either 50.3 or 75.4 MHz, for solutions in deuteriochloroform unless indicated otherwise, on a Varian Gemini 200 or a Bruker AM-300 spectrometer; chemical shifts are expressed relative to $SiMe_4$ ($\delta_H = \delta_C = 0$) with J values in Hz. Mass spectra were obtained under electron impact on a VG Autospec HR spectrometer. Dichloromethane was dried by distillation from calcium hydride. Ether refers to diethyl ether.

p-Diacetylbenzene is commercially available. Preparations of bis(*p*-acetylphenyl) ether, **13a**, bis(*p*-acetylphenyl) sulfide, **13b**, bis(*p*-acetylphenyl)methane, **13c**, bis(*p*-acetylphenyl) sulfone, **13d** and 4,4′-diacetylbiphenyl, **13e** were described in Part 1.[1] *S*-Methylthiosemicarbazidium iodide, mp 134–136 °C (from ethanol; lit., 140 °C) was obtained (74% yield) from thiosemicarbazide (46.5 g, 0.5 mol) and iodomethane (71.0 g, 0.5 mol) according to the method of Freund and Paradies.[35]

Bis(*p*-phenylacetylphenyl) ether, **5**, was prepared (yield 71%) from diphenyl ether, phenylacetyl chloride and anhydrous aluminium chloride in dichloromethane, essentially by the method of Hergenrother:[23] mp 168–169 °C (from toluene; lit.,[23] 169–170 °C); δ_H 4.35 (4 H, s, 2 × CH_2), 7.05 and 7.95 (8 H, AA′BB′, ArH) and 7.2–7.4 (10 H, m, PhH).

Bis[*p*-(2-bromo-2-phenylacetyl)phenyl] ether, 6

Bis(*p*-phenylacetylphenyl) ether, **5** (4.06 g, 10 mmol) was dissolved, with stirring, in the minimum volume of warm chloroform. The solution was then cooled and bromine (3.20 g, 20 mmol) added to it, with stirring, over 2 h. Upon complete addition the reddish brown mixture was heated under reflux for 4 h, and then evaporated under reduced pressure. The residue was dissolved in ether and the solution washed with water and aqueous sodium hydrogen carbonate, dried (Na_2SO_4) and evaporated to give a resinous product which was then sucked dry on a water-pump, giving first a foam and ultimately a fine powder (3.56 g, 63%), mp 87–89 °C (lit.,[36] 54–56 °C); δ_H($CDCl_3$/[$^2H_6$]DMSO) 6.35 (2 H, s, 2 × CHBr), 7.05 and 8.05 (8 H, AA′BB′, ArH) and 7.25–7.70 (10 H, m, PhH).

***p*,*p*′-Oxydibenzil, 7**

Method A. The bis(α-bromo ketone) **6** (11.28 g, 20 mmol) was dissolved in dimethyl sulfoxide (20 cm^3) and the reaction mixture was heated and stirred at 80 °C for 5 h. The mixture was cooled and poured into methanol (100 cm^3), and the yellow precipitate was collected, washed with methanol, water, aqueous sodium hypochlorite (to remove any residual dimethyl sulfide), water and methanol and then air-dried in a fume cupboard; yield 6.86 g (79%), mp 103–105 °C.

Method B. 48% Hydrobromic acid (8.5 cm^3, 7.5 mmol) was added dropwise over 20 min to a warm (55 °C) solution of bis(*p*-phenylacetylphenyl) ether **5** (5.08 g, 12.5 mmol) in dimethyl sulfoxide (45 cm^3). The resulting solution was stirred at 55 °C for 18 h and then poured into ice–water (400 cm^3). The resulting yellow precipitate was filtered off, washed with methanol, water, aqueous sodium hypochlorite and water again. Yield 2.04 g (38%), mp 104–107 °C (from methanol) (lit.,[22] 106.4–107.4 °C; lit.,[23] 108–109 °C); δ_H 7.36 and 8.07 (8 H, AA′BB′, *p*-C_6H_4), 7.64 (4 H, m, *m*-H in Ph), 7.83 (2 H, m, *p*-H in Ph) and 7.92 (4 H, m, *o*-H in Ph).

Bis(*p*-bromoacetylphenyl) ether, 10a

A solution of bromine (4.0 g, 25 mmol) in dichloromethane (15 cm^3) was added dropwise to a solution of bis(*p*-acetylphenyl) ether (3.2 g, 12.5 mmol) in dichloromethane (40 cm^3) heated to 30 °C. The mixture was stirred overnight at room temperature after which the solvent was distilled off and the residue was recrystallised from ethanol; yield 4.0 g (77%), mp 113–117 °C (lit.,[27] 124 °C); δ_H 4.45 (4 H, s, CH_2), 7.13 and 8.05 (2 × 4 H, AA′BB′, ArH).

4,4′-Bis(*p*-bromoacetyl)biphenyl, 10e

Bromine (4.0 g, 25 mmol) in acetic acid (15 cm^3) was added dropwise to a warm (*ca.* 50 °C) solution of 4,4′-diacetylbiphenyl (3.0 g, 12.5 mmol) in acetic acid (40 cm^3). Upon complete addition the mixture was stirred overnight at room temperature; the product was filtered off and recrystallised from chloroform; yield 2.4 g (48%), mp 212–213 °C (lit.,[37] 220–222 °C); δ_H 4.50 (4 H, s, 2 × CH_2), 7.60 and 8.10 (2 × 4 H, AA′BB′, ArH).

***p*-Bis(bromoacetyl)benzene, 9**

Bromine (4.0 g, 25 mmol) in acetic acid (15 cm^3) was added dropwise to a warm solution (*ca.* 40 °C) of 1,4-diacetylbenzene

(2.0 g, 12.5 mmol) in acetic acid (40 cm^3). After *ca.* 4 h at room temperature, the crystalline product was filtered off and washed with ethanol; yield 2.40 g (60%), mp 168 °C (from ethanol; lit.,[24] 173 °C); δ_H 4.45 (4 H, s, 2 × CH_2) and 8.10 (4 H, s, ArH).

Attempted oxidation of bis(bromoacetyl) compounds using dimethyl sulfoxide[27]

Solutions of the bis(bromoacetyl) compounds (12.5 mmol) in dimethyl sulfoxide (15 cm^3) were left at room temperature for 24 h after which they were poured into ice–water and stirred for 1 h: no precipitate appeared, as the literature indicated. The reaction was repeated using various amounts of dimethyl sulfoxide (20–100 cm^3) and different temperatures (room temp.–80 °C), but work-up with various solvents (ether, dichloromethane, chloroform) gave material, the proton resonances of which corresponded to those of the starting material.

Oxidation of the bis(bromoacetyl) compounds using dimethyl sulfoxide and hydrobromic acid

48% Hydrobromic acid (17 cm^3) was slowly added to a stirred solution of the bis(bromoacetyl) compound (25 mmol) in dimethyl sulfoxide (85 cm^3) at 55 °C; stirring was continued and the reaction was monitored by TLC. When the starting material was consumed, the solution was poured on to ice and the solid product was filtered off and dried. The melting points of the products, however, were substantially different (> 30 °C) from the literature values; the method was not further investigated.

Attempted oxidation of bis(bromoacetyl) compounds using trimethylamine *N*-oxide

The bis(bromoacetyl) compound (25 mmol) was added to a solution of anhydrous trimethylamine *N*-oxide[29] (3.75 g, 50 mmol) in chloroform (25 cm^3), and the mixture was stirred for 1 h. The yellow precipitate was filtered off, treated with dilute sulfuric acid (1 mol dm^{-3}; 25 cm^3) and then recrystallised from water. However, the products were not the desired bis(glyoxals), as was seen from the melting points (> 100 °C too high), TLC and ^1H NMR spectra, which showed peaks at δ_H 12, indicating the possible presence of a carboxylic acid group. Variation of the volume of solvent, the reaction temperature (room temp.–50 °C), and the volume of acid added led to no significant improvement.

Attempted oxidation of the bis(bromoacetyl) compounds using pyridine *N*-oxide

The bis(bromoacetyl) compound (6.6 mmol) was added to pyridine *N*-oxide (1.25 g, 13 mmol) in acetonitrile (15 cm^3) and the mixture was stirred for 3 h. Over this period the solution became yellow and a yellow precipitate formed. After the mixture had been treated with aqueous sodium hydroxide (1 mol dm^{-3}; 20 cm^3) and stirred for a further 30 min, the precipitate was centrifuged out and recrystallised from water. Again it was found that the products were very high-melting. Variation of the solvent (chloroform, water, dichloromethane), reaction temperature (room temp.–80 °C), reaction duration (20 min–3 h), and the amounts of sodium hydroxide and pyridine *N*-oxide added, had no significant effect, and the method was not further explored.

2,8-Diacetyldibenzofuran 16a

The following one-step procedure is more convenient, and gives higher yields, than the previously published two-stage method.[38] Aluminium chloride (17.33 g, 130 mmol) was added in small portions over 1 h to a well-stirred solution of acetyl chloride (10.2 g, 8.9 cm^3, 130 mmol) in 1,2-dichloroethane (50 cm^3). A solution of dibenzofuran (8.40 g, 50 mmol) in 1,2-dichloroethane (20 cm^3) was then added dropwise to the mixture during 30 min, with warming to 50 °C. The mixture was heated under reflux for 12 h, cooled to 30 °C, and poured slowly into ice–water (100 cm^3). Concentrated hydrochloric acid (20 cm^3) was added to the mixture which was then stirred for a further 1 h. The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 25 cm^3). The combined extracts were dried and evaporated, and the residue was recrystallised from ethanol (with charcoal) to give 2,8-diacetyldibenzofuran (11.3 g, 90%), mp 157–158 °C (lit.,[38] 160 °C); δ_H 2.61 (6 H, s, 2 × Me), 6.65 (2 H, d, *J* 9.0, 4- and

Table 1 Bis(glyoxals) obtained by oxidation of diacetyl substituted aromatic compounds using DMSO–HBr

Compd. no.	Yield (%)	Mp (decomp.) (°C) (lit. mp)	ν_{max}/cm^{-1} (C=O)	^1H chemical shifts (δ_H, [$^2H_6$]DMSO)				
				$CH(OH)_2$	OH	2-H/6-H	3-H/5-H	CH_2
8a	18	150–156 (160–162;[18] 110–111;[24] 144–147[27])	1687	5.71	3.60	—8.28s—		
14a	59	141–144 (140.5–142;[23] 124–127[27])	1686	5.71	6.20	8.17	7.15	
14b	98	124–128 (129–130[18])	1685	5.68	6.91	8.10	7.51	
14c	55	99–105 (102–104[27])	1686	5.80	4.25	8.03	7.32	4.16
14d	66	135–136 (138–139[40])	1685	5.68	3.50	8.15*	8.08*	
14e	91	154–157 (150;[27] 130–145[37])	1685	5.74	6.84	8.20	7.92	
17a	84	133–135§	1687	5.86	6.82	—†—		
17b	60	85–89¶	1686	5.70	6.82	—‡—		

* Provisional assignments. † δ_H 7.89 (2 H, d, *J* 9.0, 4- and 6-H), 8.35 (2 H, dd, *J* 9.0 and 2.0, 3- and 7-H) and 9.01 (2 H, d, *J* 2.0, 1- and 9-H); δ_C([$^2H_6$]-DMSO) 89.0 [$CH(OH)_2$], 111.9 (C-4 and -6), 123.3 (C-9a and -9b), 123.5 (C-1 and -9), 129.6 (C-2 and -8), 129.8 (C-3 and -7), 158.7 (C-4a and -5a) and 195.3 (C=O). ‡ δ_H 7.54 (2 H, d, *J* 8.0, 4- and 6-H), 8.17 (2 H, dd, *J* 8.0 and 2.0, 3- and 7-H) and 8.48 (2 H, d, *J* 2.0, 1- and 9-H); δ_C([$^2H_6$]DMSO) 89.2 [$CH(OH)_2$], 119.8 (C-4 and -6), 121.8 (C-9a and -9b), 125.3 (C-1 and -9), 128.6 (C-2 and -8), 129.9 (C-3 and -7), 147.3 (C-4a and -5a) and 196.0 (C=O). § Found: C, 60.7; H, 3.5. $C_{16}H_8O_5 \cdot 2H_2O$ requires C, 60.8; H, 3.8%. ¶ Not purified: used directly for the next stage.

Table 2 Bis[3-(methylsulfanyl)-1,2,4-triazines]

Compd. no.	Yield (%)	Mp (°C) (from ethanol)	Molecular formula	Found (%)			Required (%)			*m/z* $M^{+\bullet}$ (intensity, %)	Base peak (100%)
				C	H	N	C	H	N		
12	21	246–248*	$C_{14}H_{12}N_6S_2$	50.95	3.4	25.2	51.2	3.7	25.6	328 (13)	126
15a	31	186–188	$C_{20}H_{16}N_6OS_2$	57.1	3.6	20.0	57.1	3.8	20.0	420 (25)	218
15b	21	128–130*	$C_{20}H_{16}N_6S_3$	54.7	4.0	18.9	55.0	3.7	19.25	436 (24)	234
15c	28	198	$C_{21}H_{18}N_6S_2$	60.1	4.2	19.9	60.3	4.3	20.1	418 (30)	216
15d	26	223–224	$C_{20}H_{16}N_6O_2S_3$	51.15	3.2	17.6	51.3	3.4	17.9	468 (21)	149
15e	24	243–245	$C_{20}H_{16}N_6S_2$	59.25	3.9	20.6	59.4	4.0	20.8	404 (12)	178
18a	40	289–291*	$C_{20}H_{14}N_6OS_2$	57.1	3.3	19.8	57.4	3.3	20.1	418 (3)	91
18b	32	170–172 (slightly impure: see text)								434 (23)	208

* Decomp.

Table 3 NMR spectra of bis[3-(methylsulfanyl)-1,2,4-triazines]

Compd. no.	^{1}H chemical shifts (δ_H)					^{13}C chemical shifts (δ_C)								
							triazine ring			benzene ring				
	triazine 6-H	benzene 2-H/6-H	benzene 3-H/5-H	CH_3	CH_2	CH_3	C-3	C-5	C-6	C-1	C-2/C-6	C-3/C-5	C-4	CH_2
12	9.46	——8.35s——		2.76		14.0	174.2	153.2	141.8	137.0	——128.5——		137.0	
15a	9.38	8.22	7.21	2.72		13.9	173.7	153.6	141.6	160.0	119.8	128.8	129.9	
15b	9.38	8.11	7.51	2.72		13.9	173.9	153.6	141.6	140.1	128.5	131.5	132.3	
15c	9.34	8.08	7.36	2.74	4.19	13.7	173.6	154.1	141.7	145.1	127.9	129.9	131.4	41.7
15d	9.39	8.16	8.30	2.73		14.0	174.4	152.5	141.7	144.3	128.7*	128.8*	138.3	
15e	9.41	8.28	7.85	2.74		14.0	173.9	153.9	141.8	143.8	126.9	128.0	133.0	
18a	9.53	——†——		2.80		14.0	173.8	154.1	141.9	——————†——————				
18b	9.40	——‡——		2.70		14.0	173.8	154.4	141.9	——————‡——————				

* Provisional assignments. † δ_H 7.79 (2 H, d, *J* 9.0, 4- and 6-H), 8.35 (2 H, dd, *J* 9.0 and 2.0, 3- and 7-H) and 8.92 (2 H, d, *J* 2.0, 1- and 9-H). δ_C 113.1 (C-4 and -6), 121.1 (C-1 and -9), 124.8 (C-9a and -9b), 127.8 (C-3 and -7), 128.9 (C-2 and -8) and 159.4 (C-4a and -5a). ‡ δ_H 7.51 (2 H, d, *J* 8.0, 4- and 6-H), 8.01 (2 H, dd, *J* 8.0 and 2.0, 3- and 7-H) and 8.15 (2 H, d, *J* 2.0, 1- and 9-H). δ_C 120.8 (C-4 and -6), 122.0 (C-1 and -9), 124.8 (C-9a and -9b), 127.6 (C-3 and -7), 129.3 (C-2 and -8) and 148.9 (C-4a and -5a).

Table 4 Bis[3-(methylsulfinyl)-1,2,4-triazines] and bis[3-(methylsulfonyl)-1,2,4-triazines]

Compd. no.	reaction time (h)	Yield (%)	Mp (°C) (decomp.)
19a	12	52	108–110
19e	12	72	135–137
20a	3	62	208–211*
20e	5	77	80*

* *N.B.* Decomposition sets in prior to melting; **20a** ⩾ 100 °C and **20e** ⩾ 80 °C.

6-H), 7.18 (2 H, dd, *J* 9.0 and 2.0, 3- and 7-H) and 7.62 (2 H, d, *J* 2.0, 1- and 9-H).

2,8-Diacetyldibenzothiophene, 16b

This compound was similarly prepared by adding aluminium chloride (17.33 g, 130 mmol) portionwise to a solution of acetyl chloride (10.2 g, 8.9 cm^3, 130 mmol) in 1,2-dichloroethane (80 cm^3), and then adding to the mixture a solution of dibenzothiophene (9.20 g, 50 mmol) in 1,2-dichloroethane (40 cm^3), dropwise with stirring, during 30 min. Finally the mixture was heated under reflux for 16 h. Work-up gave 2,8-diacetyldibenzothiophene (9.20 g, 62%), mp 205–207 °C [from ethanol (with charcoal)] (lit.,[39] 208–209 °C); δ_H 2.65 (6 H, s, 2 × Me), 7.44 (2 H, d, *J* 2, 4- and 6-H), 8.01 (2 H, dd, *J* 8 and 2, 3- and 7-H) and 8.20 (2 H, d, *J* 2, 1- and 9-H).

Preparation of the bis(glyoxals) 8a, 14a–e and 17a–b

General procedure. 48% Hydrobromic acid (8.8 mol dm^{-3}; 17 cm^3, 150 mmol) was added dropwise with stirring over 20 min to a solution of the appropriate diacetyl compound (25 mmol) in dimethyl sulfoxide (80 cm^3) (*N.B.* Dimethyl sulfide is produced!). The mixture was heated to 60 °C at which temperature it was stirred for 18 h. After the yellow solution had been allowed to cool it was poured into ice–water (600 cm^3).

If the product was obtained at this stage as a (pale yellow) solid (compounds **14a**, **b** and **e**; **16a** and **b**), it was filtered off, washed with water and sucked dry. If the crude product did not solidify (compounds **8a**, **14c** and **d**) the aqueous mixture was extracted with ethyl acetate (3 × 200 cm^3), and the combined extracts were washed with aqueous sodium thiosulfate (10%; 300 cm^3) and water, dried ($MgSO_4$) and concentrated under reduced pressure. The bis(glyoxals) were recrystallised from dioxane–water (1:1), under which conditions they were obtained as hydrates (or partial hydrates). Their properties are collected in Table 1.

Preparation of the bis(3-methylsulfanyl-1,2,4-triazines) 12, 15 and 18

General procedure. A solution of *S*-methylthiosemicarbazidium iodide (2.33 g, 10 mmol) in the minimum volume of aqueous ethanol (50%) was added to a solution of the bis(glyoxal) (5 mmol) and sodium hydrogen carbonate (0.93 g, 11 mmol) in aqueous ethanol (50%; 30 cm^3). The mixture (in which a yellow colour was seen almost immediately) was stirred at room temperature for 48 h. The orange–yellow suspension was then extracted with dichloromethane (3 × 100 cm^3) and the combined extracts were washed with water (100 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an orange solid–foam. The bis(1,2,4-triazine) was purified by recrystallisation from ethanol.

The properties of these bis(triazines) are collected in Tables 2 and 3.

Table 5 NMR spectra of the bis[3-(methylsulfinyl)-1,2,4-triazines] **19** and the bis[3-(methylsulfonyl)-1,2,4-triazines] **20** (in [$^2H_6$]DMSO)

Compd. no.	^{1}H chemical shifts (δ_H)				^{13}C chemical shifts (δ_C)							
					triazine ring				benzene ring			
	triazine 6-H	aromatic 2-H/6-H	aromatic 3-H/5-H*	CH_3	C-3	C-5	C-6	CH_3	C-1	C-2/C-6	C-3/C-5	C-4
19a	10.28	8.12	8.58	3.12	173.4	156.0	148.9	39.6	166.1	121.6	128.0	130.0
19e	10.38	8.08	8.42	3.16	173.4	153.8	148.9	39.7	143.4	128.0	129.3	132.3
20a	10.47	8.13	8.60	3.66	166.0	155.9	148.7	39.6	163.6	119.4	128.7	128.9
20e	10.43	8.18	8.32	3.60	166.1	152.9	147.8	39.6	143.2	127.3	128.1	127.5

Oxidation of the bis(3-methylsulfanyl-1,2,4-triazines)

Preparation of the bis(sulfoxides) 19a and e. General procedure. *m*-Chloroperbenzoic acid (2.13 mol equiv.) was added (in one portion) to an ice-cooled solution (0 °C) of the bis(3-methylsulfanyl-1,2,4-triazine) (1.2 mmol) in dry dichloromethane (10 cm^3). The reaction mixture was stirred at room temperature, with exclusion of moisture, for 12 h, after which it was concentrated under reduced pressure and the residue stirred in dry ether (30 cm^3) for 10 min. The resultant pale yellow solid was filtered off, washed with dry ether and then sucked dry at the pump. Purification was effected by chromatography on silica gel with tetrahydrofuran–ethyl acetate (1 : 10) as eluent.

Preparation of the bis(sulfones) 20a and e. The same procedure as that described was followed, except that double the quantity of *m*-chloroperbenzoic acid was used; the product consisted of a mixture in which the sulfone : sulfoxide ratio was *ca.* 3 : 1 (by ^{1}H NMR).

The preferred synthesis of the bis(sulfones) is as follows.

A solution of the bis(sulfide) (500 mg) in chloroform (10 cm^3) was added dropwise with stirring to a slurry formed from wet alumina (containing 10% water by weight; 2 g) and oxone®; (6 mol equiv.) in chloroform (20 cm^3). The mixture was heated under reflux until no bis(sulfide) remained (by TLC : ether–light petroleum, 1 : 1). The mixture was cooled to room temperature and filtered and the solid residue was washed with chloroform (10 cm^3); the combined filtrate and washings were evaporated under reduced pressure and the resulting pale yellow product was chromatographed on silica gel [tetrahydrofuran–ethyl acetate (1 : 10) as eluent].

The properties of the bis(sulfoxides) and bis(sulfones) are collected in Tables 4 and 5.

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