# A comparison of some pyrolysis reactions of benzotriazoles, benzisoxazolones and benzisothiazolones

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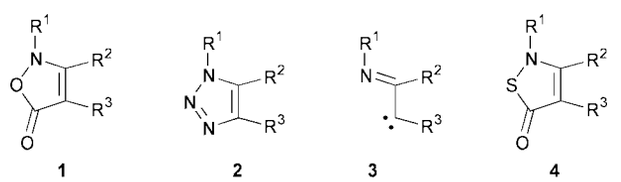
***Received (in Cambridge, UK) 16th June 2000, Accepted 31st July 2000***
***First published as an Advance Article on the web 7th September 2000***

The products of flash vacuum pyrolysis of *N*-acetyl, *N*-methyl, *N*-benzyl and *N*-heteroaryl-substituted benzotriazole, 2,1-benzoxazol-3-one and 2,1-benzothiazol-3-one have been compared. The pyrolysis of benzotriazoles and benzisoxazolones appears to involve an iminocarbene intermediate, although the *N*-benzyl analogues react by radical pathways. Benzisothiazolones appear to form iminoketene intermediates.

## Introduction

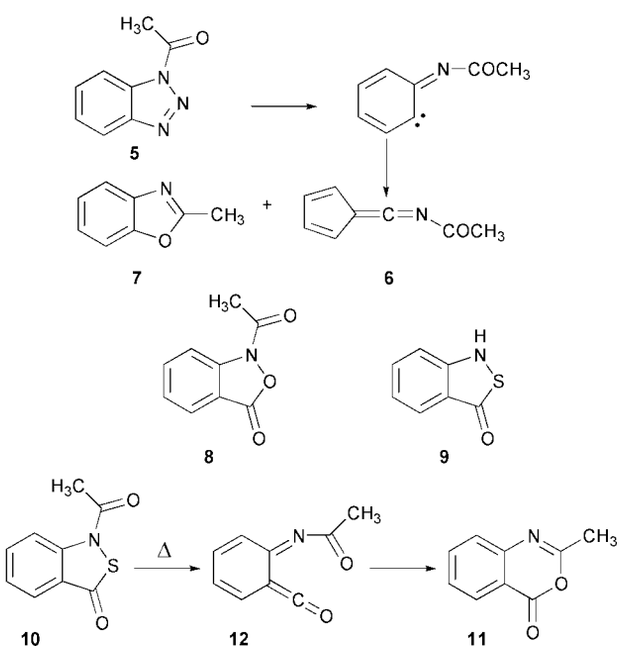
We have commented previously in a general way[1] that the thermal or photochemical decomposition of isoxazol-5(2*H*)-ones **1** is analogous to that of triazoles **2**, in that they could




both be expected to be sources of iminocarbenes **3**.[2] The reported reactions of carbenes **3** from triazoles have generally involved intramolecular rearrangements,[3,4] while those from isoxazolones have been both intramolecular[1,5,6] and intermolecular[7,8] in nature. We have recently compared the results of flash vacuum pyrolysis (FVP) of *N*-benzylbenzotriazoles and *N*-benzylbenzisoxazolones,[9] and the related acyl derivatives,[10] where the modes of decomposition were substantially different. On the other hand, the pyrolytic decomposition of isothiazolones **4** has not been studied, but such reactions could also be expected to generate the same carbene **3**. In this paper we report some comparisons of these three ring systems, concentrating on the reactions of the benzo annelated derivatives.

## Results and discussion

Wentrup and co-workers[11] studied the FVP of 1-acetylbenzotriazole **5** at various temperatures, reporting the major product at lower temperatures to be the cyclopentadiene **6**, with increasing amounts of the benzoxazole **7** at higher temperatures, the maximum yield of the latter being only 24%. Reaction of benzisoxazolone with acetyl chloride gave the *N*-acetyl compound **8** in almost quantitative yield. FVP at 590 °C gave the benzoxazole **7** in over 90% yield. The acetylation of benzisothiazolone **9** with acetyl chloride in pyridine has been reported to occur exclusively on oxygen[12,13] and it was assumed that rearrangement to the *N*-acetyl derivative **10** was followed by immediate decomposition. While this is true in basic media, in the absence of base the desired *N*-acetyl compound is readily available without contamination. Pyrolysis of **10** gave the 3,1-oxazinone **11** in high yield, contaminated only with a little *N*-acetylanthranilic acid, which we believe to arise during the isolation process. Davis *et al.*[13] also isolated **11** from reaction of **9** with acetyl chloride, and concluded that the iminoketene **12** was unlikely to be an intermediate in his reactions. However, in view of the subsequent products obtained with the benzisothiazolones below, we believe our products, including sulfur, are best rationalised in terms of the intermediate **12**, as shown in Scheme 1.




**Scheme 1**

The pyrolysis of some 1-alkylbenzotriazoles has been reported by Storr and co-workers,[14] but that of the 1-methyl analogue was not included. 1-Methylbenzotriazole **13** gave 1,3,5-triphenylhexahydro-1,3,5-triazine **14** in 89% yield when subjected to FVP: this product is expected from the trimerisation of formaldehyde phenylimine[15,16] (Scheme 2). FVP at 600 °C of *N*-methylbenzisoxazolone **15** generated a single product in good yield, which was identical to the triazine **14**, and whose structure was confirmed by a single crystal X-ray analysis, the structure being identical with that recorded in the Cambridge Crystallographic Data Centre.

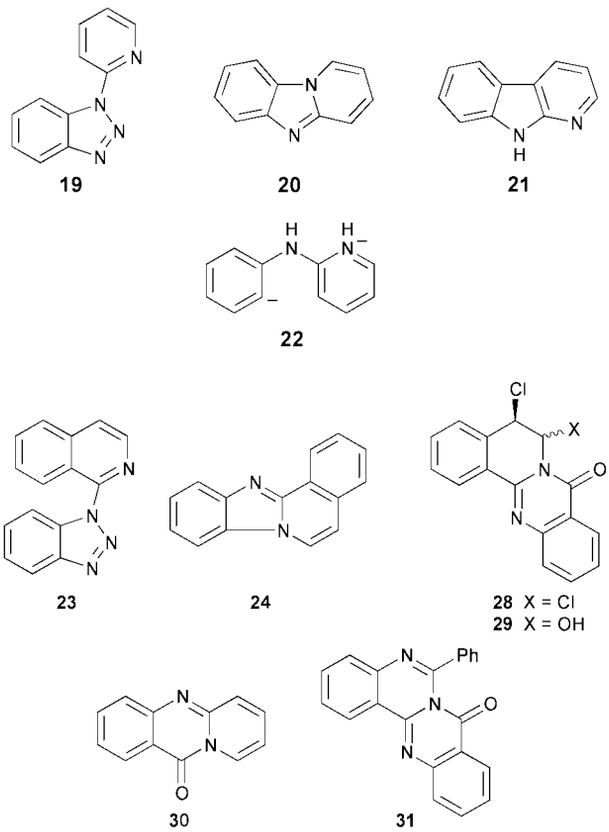
 DOI: 10.1039/b004825i

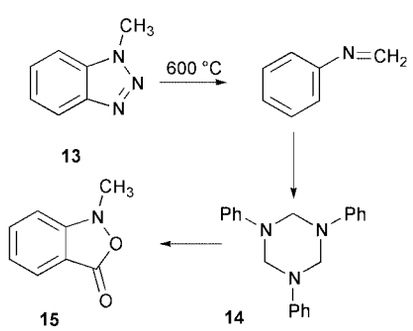
The *N*-methylbenzisothiazolone **16** appeared to be more thermally stable than **15**, but did undergo complete reaction at 700 °C. The product was a complex mixture, from which the two major products were isolated by chromatography. These were identified by GC-MS and $^{1}$H and $^{13}$C NMR comparison with authentic samples as 2,1-benzothiazole (**17**, 20%) and 1,3-benzothiazole (**18**, 5%) .We suggest these products arise by the pathway shown in Scheme 3, involving the loss of CO from the first formed iminoketene. However, in view of the low yields of characterised products, it is not possible to claim this as the major fragmentation pathway.

Whereas the pyrolysis of 1-benzyltriazole gives benzaldehyde *N*-phenylimine[14] or bibenzyl[2] depending on reaction conditions in a process believed to involve radical intermediates, the major product from the FVP of *N*-benzylbenzisoxazolone and *N*-benzylbenzisothiazolone was bibenzyl (75%). Thus the presence of an *N*-benzyl group biases thermal fragmentation in all three species towards a radical pathway.

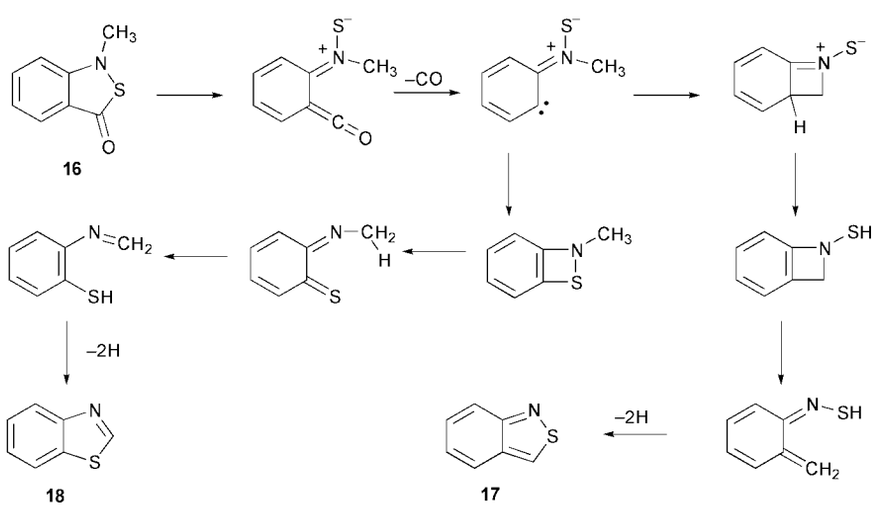
We have reported that isoxazolones substituted on nitrogen with heterocyclic substituents undergo clean and efficient pyrolysis and capture of the iminocarbenes to give imidazoles.[1,5] Accordingly, it appeared that a comparison of pyrolyses of *N*-heteroarylbenzotriazoles, benzisoxazolones and benzisothiazolones would be mechanistically more informative. Hubert[17] observed that upon irradiation at 254 nm, the 2-pyridylbenzotriazole **19** lost nitrogen to give the imidazole **20** (70%), presumed to be by rearrangement of the diradical, but equally consistent with a carbene pathway. However, when **19** was heated in phosphoric acid (the Graebe–Ullmann reaction[18]), the product was the isomeric pyridoindole **21**. This product may represent the product of electrophilic substitution within the dication **22**. Pyrolyses of **19** and analogues in boiling biphenyl were unsuccessful.[19]

We have examined the FVP of **19** and the isoquinoline analogue **23**, and observed the formation of the imidazoles **20** and **24** in nearly quantitative yields, suggesting that the Graebe–Ullmann reaction is not a pyrolytic reaction of the free triazole. Benzisoxazolone is considerably less nucleophilic than benzotriazole, and neither the isoxazolone nor its sodium salt reacted readily with 1-chloroisoquinoline. In 1,2-dimethoxyethane at 80 °C, most of the benzisoxazolone decomposed, and 80% of the 1-chloroisoquinoline was recovered, but it was possible to isolate 5% of the chloroisoquinoquinazolone **25**, which was probably formed in the same way as it was from the benzisothiazolone, detailed below. Similarly, we were unable to isolate the desired *N*-arylated compound **26** from the reaction of benzisothiazolone **9** with 1-chloroisoquinoline when it or its sodium salt were heated with the isoquinoline in ethanol or *N*,*N*-dimethylformamide, but after 20 hours in 1,2-dimethoxyethane at 80 °C, two products could be isolated. The major product (22%) was identified as the isoquinoquinazolone **27**, and the minor product (10%) was the 5-chloro analogue **25**. The $^{1}$H NMR spectrum of the latter showed a one proton singlet at $\delta$ 8.7, consistent with substitution at C-5 or C-6, but since the reported mp of the 6-chloro compound is 148 °C[20] and not



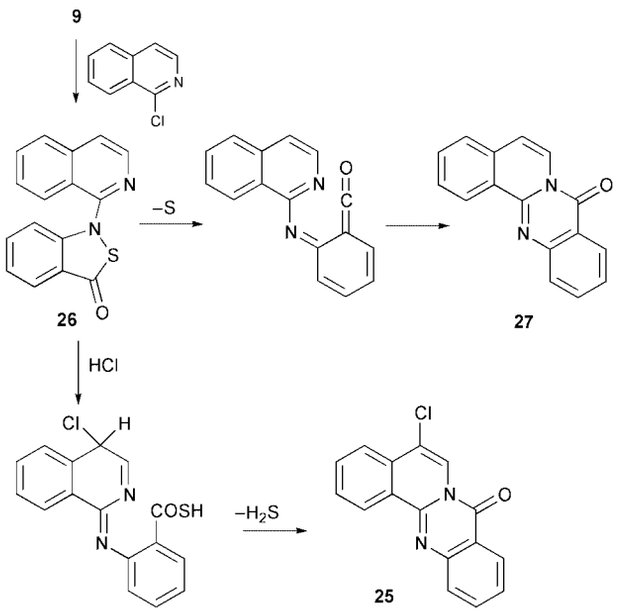




**Scheme 2**




**Scheme 3**

221 °C as observed for our compound, the structure **25** appeared most likely. This was confirmed by reaction of **27** with chlorine, which gave a mixture of the *cis* and *trans* dichloro compounds **28** in the ratio of 1 : 5. The isomers had similar vicinal coupling constants for H-5 and H-6 (*J* 3.0 and 2.5 Hz, respectively), and the structural assignments rest on the chemical evidence that follows. Reaction of the mixture with triethylamine in 1,2-dimethoxyethane caused dehydrochlorination of the *cis* isomer to give **25,** and the *trans* isomer to revert to **27**. When the pure *trans* isomer was treated with sodium hydroxide in ethanol, it gave what is presumed to be the chlorohydrin **29**, which cleanly gave **25** on reaction with acid. The products **25** and **27** are believed to arise by the processes summarised in Scheme 4. There is an alternative pathway for the formation of




**Scheme 4**

**27**, based on the work of Davis *et al.*,[13] who found that **9** reacted with pyridine to give **30** in poor yield, a reaction which involves initial nucleophilic attack of the pyridine at the carbonyl group. Because of the lower nucleophilicity of 1-chloroisoquinoline, this pathway appears less likely. However, when **9** was heated with isoquinoline at 80 °C, **27** was obtained in 75% yield. An analogous reaction of **9** with 4-chloro-2-phenylquinazoline gave the product **31** in good yield, suggesting this to be a general method for the formation of annelated quinazolines. Some support for the validity of Scheme 4 was obtained by the observation that when **9** was treated with 1-chloroisoquinoline in the presence of excess of hydrogen chloride, the yield of **25** increased somewhat, and no **27** was formed.

In conclusion, it appears that the thermal decomposition of benzotriazoles and benzisoxazolones probably proceeds through iminocarbene intermediates. That of benzisothiazolones generally proceeds *via* an iminoketene by loss of sulfur, which may then undergo decarbonylation. Pyrolysis of the isoxazolones generally proceeds at lower temperatures than the corresponding triazoles, often leading to cleaner products.

## Experimental

General experimental details have been detailed in a previous paper.[21]

### 1-Acetyl-2,1-benzoxazol-3(1*H*)-one, 8

The method of Bamberger and Pyman[22] was found to be inadequate. Acetyl chloride (2 mL) was added to a suspension of benzisoxazolone (800 mg) in dry dichloromethane at 20 °C, and the mixture stirred for 2.5 h. The solvent was removed, and the product recrystallised as colourless needles (996 mg, 95%), mp 116–118 °C (EtOH) (lit.[22] 117–118 °C) (Found: $M^{+\bullet}$, 177.0427. $C_9H_7NO_3$ requires *M* 177.0426); $\nu_{max}/cm^{-1}$ 1767, 1699, 990; $\delta_H$ 2.51 (3H, s), 7.40 (1H, dd, *J* 8, 1), 7.99 (1H, td, *J* 8, 1), 7.89 (1H, td, *J* 8, 1), 8.10 (1H, dd, *J* 8, 1); $\delta_C$ 22.1 (q), 111.6 (s), 114.7 (d), 125.6 (d), 125.7 (d), 136.6 (d), 144.7 (s), 163.3 (s), 165.5 (s).

### Flash vacuum pyrolysis of *N*-acetyl-2,1-benzoxazolone

Compound **8** (70 mg) was pyrolysed at 590 °C (100 °C, 0.05 mm, 30 min) to yield 2-methyl-1,3-benzoxazole (**7**) (51 mg, 95%) as a colourless oil, identified by comparison of its GC-MS and spectral properties with those of an authentic sample.

### 1-Acetyl-2,1-benzothiazol-3(1*H*)-one, 10

Acetyl chloride (330 mg, 1.4 eq.) was added dropwise to a stirred suspension of 2,1-benzothiazol-3(1*H*)-one[23] (480 mg) in dichloromethane (25 mL), and the mixture refluxed for 30 min. After cooling, the filtrate was evaporated to dryness and the product crystallised as an off-white solid (480 mg, 75%), mp 183 °C ($CH_2Cl_2$) (Found: C, 55.6; H, 3.95; N, 7.05%. $C_9H_7NO_2S$ requires C, 55.9; H, 3.65; N, 7.25%); $\nu_{max}/cm^{-1}$ 1705, 1660, 1620, 1600; $\delta_H$($CDCl_3$–TFA) 2.50 (3H, s), 7.3–7.9 (3H, m), 8.6 (1H, d, *J* 4.0); $\delta_C$ 25.6 (q), 119.6 (d), 123.6 (d), 124.6 (d), 124.7 (s), 135.3 (d), 147.7 (s), 167.5 (s), 186.4 (s).

### Flash vacuum pyrolysis of 10

Compound **10** (190 mg, 1 mmol) was pyrolysed at 550 °C (110 °C, 0.01 mm). Chromatographic separation on silica gel ($CH_2Cl_2$) gave two fractions. 2-Methyl-4*H*-3,1-benzoxazin-4-one, **11** (130 mg, 80%), was eluted first, mp 78–80 °C (lit.[24] 79 °C), whose structure was confirmed by its spectral properties.[25]

The second fraction was identified as *N*-acetylanthranilic acid (6%), mp 184 °C (lit.[26] 185 °C), by direct comparison with an authentic sample.

### Flash vacuum pyrolysis of 1-methylbenzotriazole, 13

The triazole **13**[27] (240 mg, 1.8 mmol) was pyrolysed at 700 °C (150 °C, 0.01 mm) to produce a colourless solid (168 mg, 89%), mp 138 °C (lit.[16] 138 °C), identified as 1,3,5-triphenylhexahydro-1,3,5-triazine **14** by comparison of its spectral properties with an authentic sample.

### Flash vacuum pyrolysis of 1-methyl-2,1-benzoxazolone, 15

The isoxazolone **15** was prepared by the method of Bamberger and Pyman.[22] $\delta_H$ 3.3 (3H, s), 7.12 (1H, dd, *J* 8, 1), 7.23 (1H, dt, *J* 8, 1), 7.64 (1H, dt, *J* 8, 1), 7.77 (1H, dd, *J* 8, 1); $\delta_C$ 42.8 (q), 111.4 (d), 112.9 (s), 124.1 (d), 125.6 (d), 135.1 (d), 158.4 (s), 167.8 (s).

The isoxazolone (100 mg) was pyrolysed at 600 °C (100 °C, 0.05 mm, 15 min) to give **14** as a colourless solid (59 mg, 75%), mp 136–138 °C (hexane), identical with the sample above; $\nu_{max}/cm^{-1}$ 1598, 1495, 1225; $\delta_H$ 4.91 (2H, s), 6.88 (1H, m), 7.03 (2H, m), 7.23 (2H, m); $\delta_C$ 68.6 (t), 117.7 (d), 120.9 (d), 129.2 (d), 148.6 (s). A single crystal X-ray analysis gave identical data to that stored in the Cambridge Crystallographic Data Centre.

### Flash vacuum pyrolysis of 1-methyl-2,1-benzothiazol-3(1*H*)-one, 16

Compound **16**[28] (0.4 g, 2.4 mmol) was pyrolysed at 700 °C (150 °C, 0.01 mm) and the products separated by column chromatography (silica, $CH_2Cl_2$). 2,1-Benzothiazole, **17** (0.09 g, 28%), was isolated first, identified by its $^1H$ and $^{13}C$ NMR spectra,[29] followed by 1,3-benzothiazole **18**, (0.04 g, 12%), identified by comparison with a commercial product.

### Flash vacuum pyrolysis of 1-benzyl-2,1-benzoxazolone

Flash vacuum pyrolysis of 1-benzyl-2,1-benzoxazolone[30] (80 mg) at 700 °C in the usual way gave four fractions after chromatography. The first was 1,2-diphenylethane, mp 50–52 °C (30 mg, 91%). The three minor fractions could not be identified.

### Flash vacuum pyrolysis of 1-benzyl-2,1-benzothiazol-3(1*H*)-one

A solution of **9** (151 mg, 1 mmol), benzyl chloride (1.3 eq.) and sodium methoxide (1.3 eq.) in methanol was refluxed for 14 h under nitrogen. The solvent was removed and the ether soluble fraction purified by chromatography (silica/$CH_2Cl_2$) to give the title product (105 mg, 44%), mp 52 °C (lit.[28] 54–55 °C). $\delta_C$(10 s delay) 52.4 (t), 112.4 (d), 119.7 (d), 122.1 (s), 124.0 (d), 127.4 (d), 128.3 (d), 128.8 (d), 133.9 (d), 135.4 (s), 153.6 (s), 189.3 (s). Flash vacuum pyrolysis of the compound at 700 °C (150 °C, 0.01 mm, 20 min) gave 1,2-diphenylethane (95%), mp 50–52 °C (lit.[31] 52 °C) as the sole identifiable product. The structure was confirmed by GC-MS comparison with an authentic sample.

### Flash vacuum pyrolysis of 19

Triazole **19**[19] (300 mg) was pyrolysed at 700 °C (120 °C, 0.01 mm, 30 min) to give pyrido[1,2-*a*]benzimidazole **20** (165 mg, 64%), mp 179 °C (lit.[17] 179 °C), characterised by its spectral properties. $\delta_C$ 110.0 (d), 110.2 (d), 117.6 (d), 120.8 (d), 125.0 (d), 125.4 (d), 129.1 (d), 144.1 (s), 148.1 (s).

### Flash vacuum pyrolysis of 23

Triazole **23**[32] (120 mg), prepared by the method of Hubert and Reimlinger,[19] was pyrolysed at 600 °C (120 °C, 0.01 mm, 30 min) to give benzimidazo[2,1-*a*]isoquinoline **24** (97 mg, 91%), mp 131 °C (lit.[17] 130 °C), characterised by its spectral properties. $\delta_C$ 109.6 (d), 110.9 (d), 119.5 (d), 120.9 (d), 121.5 (d), 123.1 (s), 124.4 (d), 124.6 (d), 126.7 (d), 127.8 (d), 129.6 (d), 129.7 (s), 131.2 (s), 143.4 (s), 146.8 (s).

### Reaction of 9 with 1-chloroisoquinoline

A solution of **9** (230 mg) and 1-chloroisoquinoline (280 mg, 1 eq.) in 1,2-dimethoxyethane (20 mL) was refluxed under nitrogen for 20 h. The mixture of products was washed with $NaHCO_3$ and chromatographed on silica ($CH_2Cl_2$). The first product was 5-chloro-8*H*-isoquino[1,2-*b*]quinazolin-8-one, **25** (40 mg, 10%), mp 221 °C ($CH_2Cl_2$) (Found: C, 68.3; H, 3.1; N, 10.1%. $C_{16}H_9ClN_2O$ requires C, 68.45; H, 3.2; N, 10.0%); $\nu_{max}$/$cm^{-1}$ 1695, 1640, 1605; $\delta_H$ 7.5–8.05 (6H, m), 8.3–8.5 (1H, m), 8.7 (1H, s), 8.9–9.1 (1H, m); $\delta_C$ 117.4 (s), 120.1 (d), 120.8 (s), 123.9 (d), 126.4 (d), 127.3 (d), 127.4 (d), 127.7 (d), 129.6 (d), 131.4 (s), 132.5 (d), 135.3 (d), 145.1 (s), 146.7 (s), 158.3 (s).

The second product was 8*H*-isoquino[1,2-*b*]quinazolin-8-one, **27** (80 mg, 22%), mp 197 °C (lit.[32] 197 °C); $\delta_C$(10 s delay) 113.0 (d), 117.6 (s), 121.7 (d), 125.6 (d), 126.3 (d), 127.1 (d), 127.2 (s), 127.3 (d), 128.3 (d), 132.0 (d), 132.7 (s), 134.7 (d), 145.9 (s), 147.3 (s), 159.2 (s). Compound **27** was the major product (75%) when **9** was reacted with isoquinoline as above.

### 5,6-Dichloro-5,6-dihydro-8*H*-isoquino[1,2-*b*]quinazolin-8-one, 28

Gaseous chlorine was bubbled through a solution of **27** (50 mg) in $CH_2Cl_2$ for 15 min and the solvent was then evaporated. NMR analysis indicated the presence of two diastereomers in the ratio of 5:1. Chromatography on silica ($CH_2Cl_2$) gave the *trans* isomer of the title compound (30 mg, 47%) as colourless crystals, mp 76 °C (pentane) (Found: $M^+$, 316.0166. $C_{16}H_{10}{}^{35}Cl_2N_2O$ requires *M* 316.0170). $\nu_{max}$/$cm^{-1}$ 1695, 1640, 1600; $\delta_H$ 5.47 (1H, d, *J* 2.5), 7.37 (1H, d, *J* 2.5), 7.6–7.9 (6H, m), 8.3–8.6 (2H, m); $\delta_C$ 55.3 (d), 64.3 (d), 120.3 (s), 127.5 (d), 127.8 (d), 128.2 (d), 128.6 (d), 128.8 (d), 130.6 (d), 132.7 (s), 132.8 (d), 135.4 (d), 145.5 (s), 147.1 (s), 160.5 (s). The minor *cis* isomer could not be isolated in a pure state.

### Dehydrochlorination of 28

(i) A mixture of *trans*-**28** (160 mg), sodium hydroxide (400 mg), ethanol (8 mL) and water (7 mL) was refluxed for 1 h. After removal of solvent, the residue was boiled for 3 min with a mixture of ethanol and 15% HCl (1:1, 30 mL). The solvent was evaporated, the residue dissolved in dichloromethane, and the solution was washed with $NaHCO_3$. The organic product (100 mg, 74%) was identical in all respects with the sample of **25** obtained above. (ii) When the 5:1 mixture of *trans*- and *cis*-**28** was reacted with triethylamine in 1,2-dimethoxyethane for 1 h at 80 °C, the product contained a 5:1 mixture of **27** and **25** ($^1$H NMR analysis).

### 6-Phenyl-8*H*-quinazolino[4,3-*b*]quinazolin-8-one, 31

Reaction of **9** with 4-chloro-2-phenylquinazoline as described above produced the title compound (80%), mp 292 °C (lit.[33] 292 °C). $\delta_H$($CDCl_3$–$CF_3CO_2H$) 7.5–8.3 (m, 12H), 8.9 (d, *J* 4, 1H); $\delta_C$($CDCl_3$–$CF_3CO_2H$) 113.2 (s), 118.0 (s), 120.5 (d), 125.6 (d), 127.7 (d), 128.5 (d), 128.9 (d), 129.0 (d), 129.7 (d), 131.5 (d), 132.0 (d), 138.4 (s), 137.0 (s), 138.6 (d), 139.4 (d), 143.3 (s), 150.6 (s), 156.9 (s), 176.8 (s).

## Acknowledgements

The authors are grateful to the Australian Research Council for financial support. J. A. S. acknowledges an Australian Postgraduate Award. We thank Dr M. R. Taylor for the single crystal X-ray analysis of compound **14**.

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