# 4*H*-Azepin-4-ones from 4-azidophenols in low-temperature matrices

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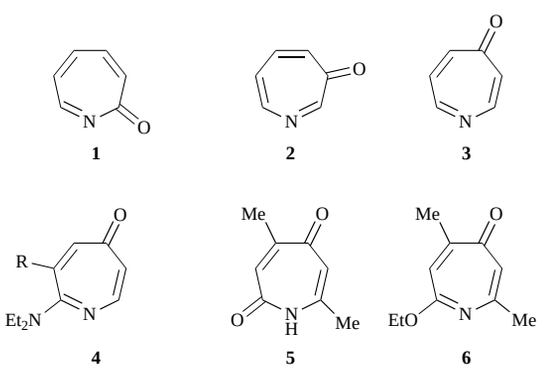
**In an attempt to develop a synthetic approach to 4*H*-azepin-4-ones in exceptionally mild conditions, 4-azidophenols have been photolysed in $N_2$ matrices at 12–14 K and subjected to flash vacuum pyrolysis (FVP) with subsequent trapping of the products in $N_2$ matrices. The reactions were followed by IR spectroscopy. The compounds studied were 4-azidophenol, which was prepared in a purer form than achieved by earlier workers, 4-azido-2-nitrophenol, the previously unknown 2,6-dichloro and 2,6-dibromo and 2-chloro-6-methyl derivatives of 4-azidophenol, and a heterocyclic analogue, 5-azido-8-hydroxyquinoline. In all cases, IR spectra indicated that the expected ring expansion to give azepinones occurred, while in some conditions intermediate hydroxyazacyclohepta-1,2,4,6-tetraenes could also be detected. For several of the azidophenols, photolyses and pyrolyses were attempted on a larger scale (50 mg or more) in a specially constructed low-temperature cell. These reactions were monitored by diffuse reflection IR spectroscopy (DRIFTS), which showed that the desired azepinones were formed at low temperature. Attempts to isolate the azepinones by warming to room temperature, however, resulted only in polymeric products. Preparative scale pyrolyses in conventional FVP equipment also gave polymers.**

## Introduction

There are three types of azepinones—aza analogues of tropone—corresponding to the three isomeric parent compounds, 2*H*-azepin-2-one **1**, 3*H*-azepin-3-one **2** and 4*H*-azepin-4-one **3**. Their chemistry has been recently reviewed.[1] Examples of all three types have been synthesized, although the parent compounds themselves seem to be unknown. By far the most common are derivatives of 2*H*-azepin-2-one **1**.



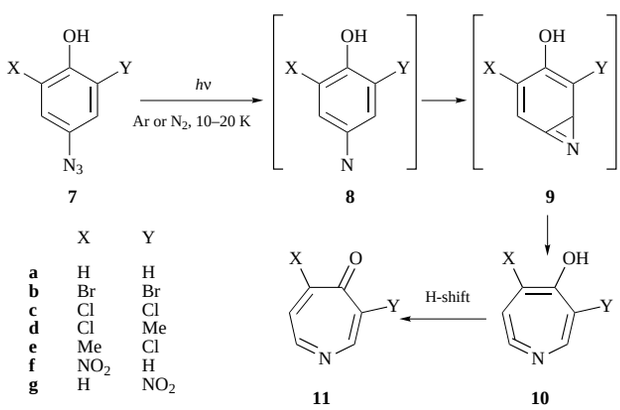
**1** **2** **3**

**4** **5** **6**

Azepin-4-ones have been particularly elusive. After an early claim,[2] which was later shown to be erroneous,[3] there have been only three papers, all appearing in 1972, reporting the synthesis of azepin-4-ones.[4–6] Diethylamino derivatives **4** (R = H or Pr$^i$) were obtained in low yields, along with azepin-2-ones, by photolysis of aryl azides in diethylamine and subsequent oxidation of the short-lived 1*H*-azepines thus generated.[4] In another approach, two groups reported that treatment of dione **5** with triethyloxonium tetrafluoroborate gave very low yields of azepinone **6**.[5,6] Some benzannelated analogues were also prepared.[6]

The paucity of known examples and the low yields obtained suggest that azepin-4-ones are generally of low stability, and the original question of whether azepinones would be aromatic, seems to have been answered negatively.[5] The azepin-4-ones so far isolated all have substituents with heteroatoms attached to the carbon of the C=N bond in the ring, and some stabilization of the system may result from this electronic arrangement. The previous work provides useful spectroscopic data (IR, UV–VIS and $^1$H NMR) to assist further studies on these compounds.

Earlier research on the photochemistry of aryl azides isolated in low temperature matrices,[7–12] including studies made in our own laboratory,[13–17] suggested a new approach to the synthesis of azepin-4-ones in exceptionally mild conditions: the low-temperature matrix photolysis of 4-azidophenols. The proposed route is shown in Scheme 1, and is based on well known matrix photochemistry of phenyl azides.




**7** **8** **9**

| | X | Y |
|---|---|---|
| **a** | H | H |
| **b** | Br | Br |
| **c** | Cl | Cl |
| **d** | Cl | Me |
| **e** | Me | Cl |
| **f** | $NO_2$ | H |
| **g** | H | $NO_2$ |

**11** **10**

**Scheme 1**

Unravelling the mechanism of the photolysis of phenyl azides has been unexpectedly complicated. The current position was reviewed recently.[18,19] The initial step involves loss of dinitrogen, giving a singlet nitrene S-**8**, which can subsequently either rearrange to an azacycloheptatetraene (didehydroazepine) **10**, or decay to the ground-state triplet nitrene T-**8**. So far, singlet nitrenes have not been detected directly in matrix or flash-photolysis studies, but triplet nitrenes are more persistent at low temperatures, and have been observed by EPR,[20–23] UV–VIS [24–28] and IR [11,14,16] spectroscopy. Once formed, the triplet nitrene can absorb a second photon and regain the singlet manifold by intersystem crossing.[11] It has thus been shown that virtually all of the original azide will be converted to the aza-

cycloheptatetraene, unless carefully selected monochromatic light is used for the photolysis.

If both positions in the benzene ring *ortho* to the azido group are substituted, the ring expansion of the phenylnitrene is suppressed.[14,16] In other cases, however, the ring expansion seems quite general, and occurs with either electron-releasing or -withdrawing substituents in the *meta* or *para* positions.[15] The intermediacy of a benzazirine **9** has not been established for the rearrangement of a singlet phenylnitrene, and a concerted pathway from S-**8** to **10** remains a possibility, with the azirine structure in this case representing an energy maximum. On the other hand, azirines analogous to **9** have been observed in the matrix photolysis of naphthyl azides,[13] and were shown to absorb a second photon and rearrange to the corresponding benzazacycloheptatetraenes. This contrast between phenyl and naphthyl derivatives probably reveals a marked difference in stability between the two classes of azirines.

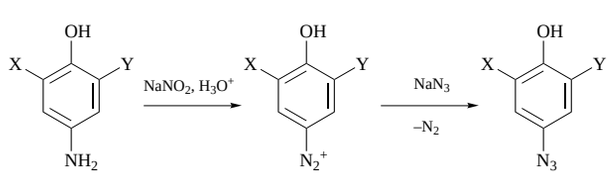
Based on these earlier discoveries, matrix photolysis of 4-azidophenols **7** should lead to the formation of hydroxy-substituted azacycloheptatetraenes **10**, which are simply enol tautomers of azepin-4-ones **11**. We concluded therefore that the matrix photolysis of 4-azidophenols should provide a convenient route to azepin-4-ones, at least in very small quantities, and that the target molecules **11** would be obtained either in the matrices directly, or by intermolecular proton exchange between molecules of **10** upon warming.

The proposed starting materials, 4-azidophenols, however, were virtually unknown. In 1907 Forster and Fierz reported the preparation of 4-azidophenol and its nitration in the presence of nitrous acid to give 4-azido-2-nitrophenol,[29] but this appears to be the only paper on 4-azidophenols published until the preliminary communication of our own work[30] in 1994. We have now discovered that at least certain types of 4-azidophenols can be prepared conveniently and have moderate stability at room temperature. In the earlier communication we reported the matrix photolysis of the 2,6-dibromo- and 2,6-dichloro-azidophenols **7b** and **7c**. In this paper we describe fully our IR studies of the matrix photolysis of six azidophenols, including the unsubstituted parent **7a**. In addition we describe matrix-isolation IR studies of the products from vacuum pyrolysis of the azidophenols and attempts to carry out the reactions to provide preparatively useful quantities (>50 mg) of azepin-4-ones.

## Results and discussion

### Synthesis and stability of azidophenols

In principle, 4-azidophenols **7** should be readily available from the corresponding 4-aminophenols **12** by diazotization followed by treatment of the diazonium salts **13** with azide anion, as outlined in Scheme 2. Only 4-azidophenol **7a** and the 2-nitro derivative **7f** had been reported previously.[29] We have found that the straightforward procedures of Scheme 2 can be applied to a



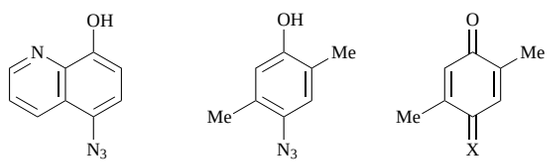

**12** **13** **7**

**Scheme 2**

number of commercially available 4-aminophenols, to give 4-azidophenols **7a–d** and **7f** in moderate yields (35–64% after purification). The intermediate hydroxydiazonium salts **13** were not isolated. 5-Azido-8-hydroxyquinoline **14** was also obtained (32%) from 5-amino-8-hydroxyquinoline in the same way.

The azidophenols vary in thermal stability, and it appears that electron-withdrawing substituents (*e.g.* Br and Cl) have a stabilizing effect, while the mildly electron-releasing methyl group is destabilizing. Forster and Fierz[29] obtained the unsubstituted parent compound **7a** as an oil, which could be frozen, but which re-melted at about 20 °C, and they remarked on its thermal instability, its sensitivity to light and the difficulty of achieving satisfactory elemental analyses. In our hands **7a** was obtained as a crystalline solid with mp 40–42 °C, and was thus appreciably purer than the sample reported previously. Nevertheless, it was still insufficiently stable to allow satisfactory elemental analysis, although IR and $^1$H NMR data confirmed its identity. In contrast, the 2,6-dibromo- and 2,6-dichloro-4-azidophenols, **7b** and **7c**, were obtained as easily purified and relatively stable, crystalline solids, for which satisfactory elemental analyses were readily obtained. 4-Azido-2-nitrophenol **7f** was similarly stable. It had been previously noticed[29] that **7f**, which survived steam distillation, was more stable thermally than **7a**, which 'decomposes profoundly when heated with water.'

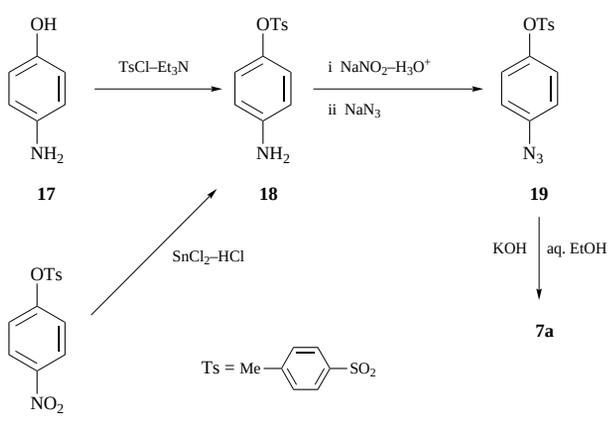
Introduction of both methyl and chloro substituents in **7d** resulted in reduced thermal stability compared with the dichloro derivative **7c**, while attempts to prepare the dimethyl derivative **15** failed completely. In the latter case, the isolated product was the dimethylquinone **16** (X = O), presumably formed by loss of a proton from the corresponding hydroxydiazonium salt (*cf.* **13**) followed by aerial oxidation of the resulting 1,4-diazoquinone **16** (X = $N_2$). Such proton loss was an expected drawback in the simple approach to 4-azidophenols which we had adopted, but fortunately turned out not to be a problem with most of the compounds tried.




**14** **15** **16**

In the case of bicyclic azidophenols, attempts to prepare 4-azido-1-naphthol from 4-amino-1-naphthol gave the corresponding diazonapthoquinone in the same way that attempts to prepare **15** gave **16** (X = O). The heterocyclic analogue, 5-azido-8-hydroxyquinoline **14**, however, was readily prepared and relatively stable, another example of electron-withdrawing substitution conferring stability.

Deprotonation of the intermediate hydroxydiazonium salts (*cf.* **13**) can be avoided by protection of the hydroxy group. Thus an alternative synthesis of 4-azidophenol **7a** was achieved as shown in Scheme 3. 4-Aminophenol **17** was selectively *O*-




**17** **18** **19**

**20**

**Scheme 3**

tosylated in the presence of triethylamine,[31] and the protected aminophenol **18** could be diazotized and treated with sodium azide, to give the protected azidophenol **19**, which was finally

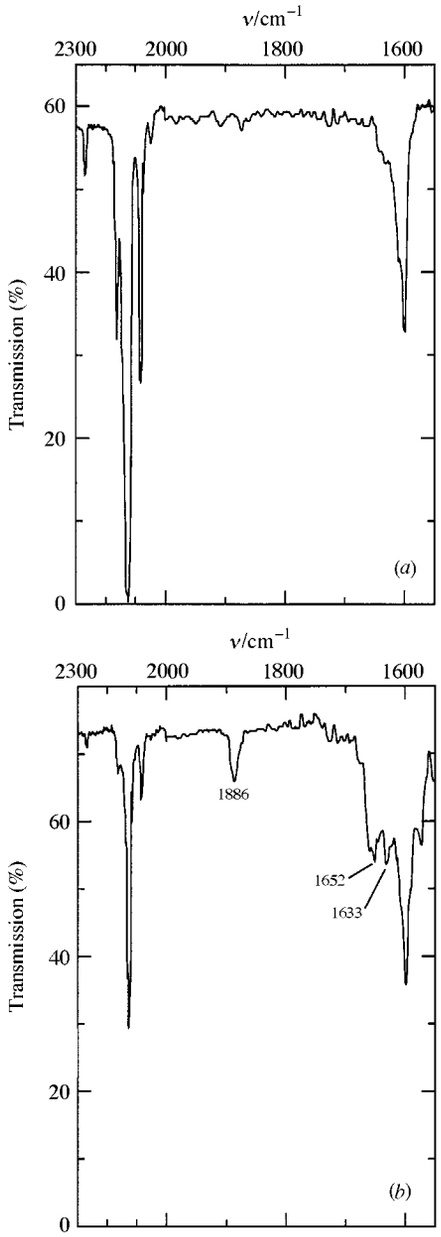



**Fig. 1** IR spectra in the region 2300–1550 $cm^{-1}$ of 4-azidophenol **7a** in a relatively dilute $N_2$ matrix at 14 K: (*a*) before photolysis, (*b*) after 60 min photolysis with $\lambda > 200$ nm

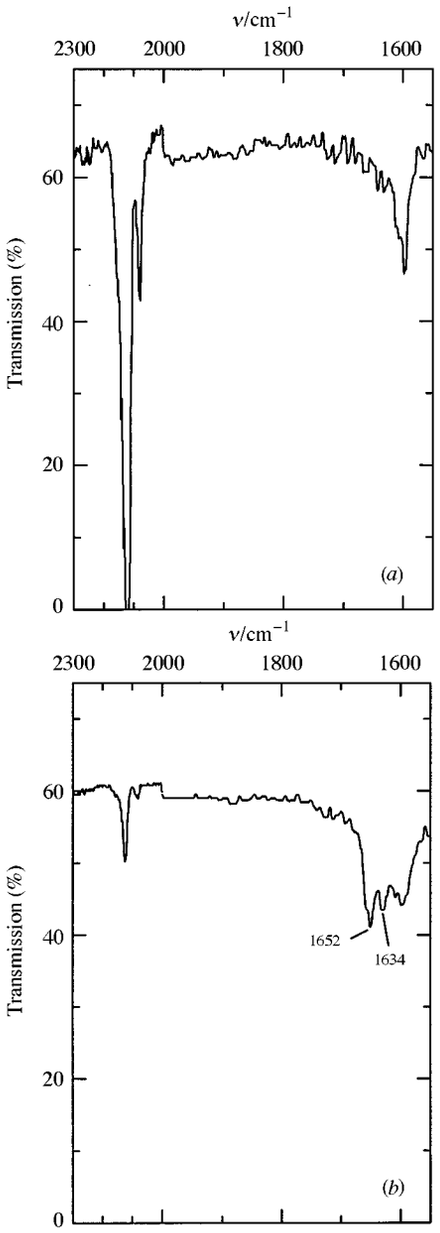



**Fig. 2** IR spectra in the region 2300–1550 $cm^{-1}$ of 4-azidophenol **7a** in a relatively concentrated $N_2$ matrix at 14 K: (*a*) before photolysis, (*b*) after 45 min photolysis with $\lambda > 200$ nm

hydrolysed with aqueous ethanolic KOH, giving **7a** in an overall yield of 60%. Alternatively, **18** could be obtained by reduction of 4-nitrophenyl tosylate (toluene-*p*-sulfonate) **20**. The application of this approach to the synthesis of 4-azido-1-naphthol failed, however: neither tosyl nor mesyl protecting groups could be removed by hydrolysis in the final step under conditions which did not also promote azide decomposition.

All the azidophenols prepared were stored in a freezer for the shortest possible time before use in the matrix experiments.

### Matrix photolysis of the azidophenols

All the 4-azidophenols prepared were trapped in $N_2$ matrices at 12–14 K and photolysed. In each experiment progress of the photolysis was monitored by IR spectroscopy. None of the azidophenols was volatile enough to be premixed with the host gas in accurately determined ratios by standard manometric techniques. Deposition of the matrices was therefore carried out by subliming the azidophenols from a side-arm attached directly to the vacuum shroud of the cold cell into a stream of the host gas controlled by a fine needle valve. In some cases it was necessary to warm the azide to promote sublimation at an appreciable rate. Matrix ratios (azidophenol : $N_2$) could not be estimated reliably with this method of deposition, but, by control of the host-gas flow rate and sample temperature during sublimation, it was possible in most cases to deposit either relatively dilute or relatively concentrated matrices. The difference in photolytic behaviour of the azidophenols in dilute and concentrated matrices proved informative.

Fig. 1 shows portions of matrix IR spectra recorded before and after photolysis of 4-azidophenol **7a** in a relatively dilute matrix, and Fig. 2 shows the equivalent spectra for a more concentrated matrix. Similar experiments were carried out several times, and the results were found to be quite consistent. Table 1 gives full IR data for the region 2500–400 $cm^{-1}$ obtained from typical experiments of this type. Absorptions in the region above 3000 $cm^{-1}$, which include the potentially significant phenolic $\nu$(OH) bands, were complicated by the presence of traces of water, which continued to be deposited on top of the matrix after deposition. The interpretation of changes in the IR spectrum in this region was therefore judged unreliable, and the data are not included in Table 1 for this reason.

The IR bands of **7a** cannot all be confidently assigned to

**Table 1** Infrared absorptions ($cm^{-1}$) in the range 2500–400 $cm^{-1}$ present before and arising after photolysis of 4-azidophenol **7a** in relatively dilute and concentrated $N_2$ matrices at 14 K [a]

| Before photolysis | | After photolysis | | Before photolysis | | After photolysis | | Before photolysis | | After photolysis | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dilute | Conc. | Dilute | Conc. | Dilute | Conc. | Dilute | Conc. | Dilute | Conc. | Dilute | Conc. |
| 2164m [b] | | | | | | 1359 | | | | | 848 |
| 2126s [b] | 2126s [b] | | | 1343m | | | | 832s | 827s | | |
| 2080s [b] | 2083m [b] | | | 1310s [f] | 1305m [f] | | | | | 824 | 830 |
| | | 1886m [c] | | 1294m [f] | | | | | | 814vw | |
| | | 1661 | | | | 1280 | 1269 | 810 | | | |
| | | 1652m [d] | 1652m [d] | 1263s | 1261s | | | | | 802vw | |
| | | 1633m [e] | 1634m [e] | | | 1251 | | 778m | 777m | | |
| 1606 | 1607 | | | | | 1238 | 1240 | | | 776m | 773m |
| 1600m | | | | 1221 | 1231 | | | 760m | 754m | | |
| | | | 1598m | 1179m | | | | | | 746 | |
| | 1593m | | | 1172 | 1169 | | | 707 | 707 | | |
| | | 1592 | | | | 1161 | 1149 | | | 696m | |
| | | 1574 | | 1154 | | | | 694 | | | |
| | | 1553 | | | | 1143 | | | | 668 | |
| | | 1536m | | 1123 | 1131 | | | | | | 642vw |
| 1511s | 1508s | | | 1105m | | | | 638s [g] | 636s [g] | | |
| 1471 | 1469 | | | | | | 1104 | | | 619 | |
| | | 1463 | | | | | 1102 | 596 | 589 | | |
| | 1461 | | | 1074 | | | | | 574 | | |
| | | 1451 | | | | | 1073 | 534m [h] | 527 [h] | | |
| 1445m | 1446 | | | | | 1030 | | 514s | | | |
| | | 1434 | | | | | 950 | | | 512m | 512m |
| 1413 | 1428 | | | | | 914 | 906 | | 509s | | |
| | | 1392 | | 891 | | | | | | 501 | |
| | | 1382m | 1377 | | | 882m | 877m | | | 466 | 465 |
| 1380 | 1376m | | | 852 | | | | 444 | | | |

[a] Bands were weak unless denoted s strong, m medium or vw very weak. [b] **7a** $\nu_a(N_3)$. [c] **10a** $\nu$(C=C=N). [d] **11a** $\nu$(C=O). [e] **11a** $\nu$(C=N). [f] **7a** $\nu_s(N_3)$. [g] **7a** $\delta$(NNN). [h] **7a** $\gamma$(NNN).

**Table 2** Azide stretching frequencies and significant photoproduct IR bands for $PhN_3$ and azidophenols in $N_2$ matrices [a]

| Compound | $\nu_a(N_3)$ [b]/$cm^{-1}$ | $\nu_s(N_3)$ [c]/$cm^{-1}$ | Photoproduct | IR absorptions ($\nu$/$cm^{-1}$) |
|---|---|---|---|---|
| $PhN_3$ [d] | 2137vs, 2112s, 2102vs, 2087s | 1305s, 1298vs | 1-azacyclohepta-1,2,4,6-tetraene | 1891m $\nu$(C=C=N) |
| **7a** | 2164m, 2126s, 2080s | 1310s, 1294m | **10a** | 1886m $\nu$(C=C=N) |
| | | | **11a** | 1652m $\nu$(C=O), 1634m $\nu$(C=N) |
| **7b** | 2126s | 1314m | **10b** | 1886m $\nu$(C=C=N) |
| | | | **11b** | 1675m, 1665m $\nu$(C=O), 1645m $\nu$(C=N) |
| **7c** | 2126s, 2080w | 1327m | **10c** | 1886m $\nu$(C=C=N) |
| | | | **11c** | 1676w $\nu$(C=O), 1648w $\nu$(C=N) |
| **7d** | 2128s, 2111w | 1320m, 1303w | **10d/10e** [e] | 1886m $\nu$(C=C=N) |
| | | | **11d/11e** [e] | 1660w $\nu$(C=O), 1645w $\nu$(C=N) |
| **7f** | 2126s, 2093w | 1307w, 1293s | **10f/10g** [e] | 1873m $\nu$(C=C=N) [f] |
| | | | **11f/11g** [e] | 1671m, 1667w $\nu$(C=O), 1625m $\nu$(C=N) |
| **14** | 2140s, 2116s | 1293w | **21/22** [e,g] | 1674s $\nu$(C=O), 1645m $\nu$(C=N) |

[a] Bands are denoted vs very strong, s strong, m medium or w weak. [b] Azide asymmetric stretch. [c] Azide pseudosymmetric stretch. [d] Data from ref. 15, included for comparison. [e] Two products possible, see text. [f] Value obtained from a pyrolysis experiment. [g] The azacycloheptatetraene was not observed with this azidophenol.

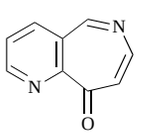
particular vibrations, but comparison with the matrix IR spectrum of $PhN_3$, which has been analysed in detail,[17] permits identification of the asymmetric and pseudosymmetric azide stretches, at 2164–2080 and 1294–1310 $cm^{-1}$, respectively, and, with slightly less certainty, the $\delta$(NNN) (in-plane) and $\gamma$(NNN) (out-of-plane) deformation modes at 638–636 and 534–527 $cm^{-1}$, respectively. As is commonly observed, the azide stretching bands are split by Fermi resonance.[17,32] Although the exact matrix concentrations of the azidophenol could not be determined, more concentrated matrices could be deposited by reducing the flow rate of the matrix host gas during deposition. Comparison of the data in Table 1 for **7a** before photolysis shows small changes in band positions, splittings and intensities on going from relatively dilute to relatively concentrated matrices. In more concentrated matrices, a higher proportion of the guest species will be present as molecular aggregates rather than as isolated molecules, and the observed changes in the IR spectrum reflect this. There was thus a noticeable tendency for IR bands to be either split or be broader and less well resolved in the more concentrated matrices.

Upon photolysis of **7a** in relatively dilute matrices, the product spectrum contained a band at 1886 $cm^{-1}$ [Fig. 1(*b*) and Table 1], which is highly characteristic of an azacycloheptatetraene, and which can therefore be assigned to the $\nu$(C=C=N) mode of **10a**. In more concentrated matrices the relative intensity of this band diminished, and at sufficiently high concentrations it no longer appeared. Instead, IR bands, including medium intensity bands at 1652 and 1634 $cm^{-1}$, which were present only at lower intensity in the dilute matrix product spectra, became more prominent [Fig. 2(*b*) and Table 1]. The band at 1652 $cm^{-1}$ is clearly a carbonyl stretching band, and falls well within the range reported for azepinones such as **6**.[5,6] It is therefore assigned to the azepinone **11a**, the expected product from tautomerization of **10a**. The band at 1634 $cm^{-1}$ is probably the $\nu$(C=N) band of the same species. With dilute matrices, attempts were made to convert **10a** into **11a** in the matrix by (*i*)

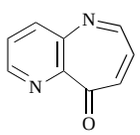
annealing at about 35 K and (*ii*) photolysis with various wavelengths of UV light, but no discernible conversion occurred. This might be expected for the non-polar and non-protic environment of the matrix. The *ν*(C=C=N) band of **10a** disappeared only when matrices containing **10a** were warmed carefully to allow controlled evaporation of the host (*ca.* 50 K). In these conditions, the final IR spectra showed considerable band broadening, but the *ν*(C=O) band of **11a** seemed to increase in intensity, as expected. The tautomerization of **10a**, therefore, most likely occurs *via* an intermolecular proton transfer.

Similar matrix IR spectra for the photolysis of the dibromo and dichloro derivatives, **7b** and **7c**, have already been published.[30] Detailed IR data for dilute and concentrated matrices, similar to those given in Table 1 for **7a**, have been obtained for **7b**, **7c** and the 2-chloro-6-methyl derivative **7d**. With all these compounds, the same dependence of photoproduct on the matrix concentration was observed, with the azacycloheptatetraenes **10** predominating in dilute matrices and the azepinones **11** predominating in more concentrated matrices, with no trace of the azacycloheptatetraenes at high enough concentrations. All experiments were repeated several times, to ensure consistency. Table 2 summarizes the important IR bands observed in these experiments, with data for $PhN_3$ included for comparison. In the case of **7d**, which is unsymmetrically substituted, there is the possibility of formation of two azacycloheptatetraenes, **10d** and **10e**, and two azepinones, **11d** and **11e**. Only one *ν*(C=C=N) band at 1886 $cm^{-1}$ was observed in the product spectrum in dilute matrices, and only one *ν*(C=O) band at 1660 $cm^{-1}$ in more concentrated matrices, but these bands, especially the former, are not likely to be very sensitive to the subtle changes in substitution between the two possible isomeric pairs, so it should not be concluded that only one azacycloheptatetraene and one azepinone were generated. A similar problem in determining whether one or two azacycloheptatetraenes were formed arose in the matrix photolysis of 3-substituted phenyl azides.[15]

The 2-nitro derivative **7f** and the quinoline derivative **14** were less volatile than the other azidophenols studied. They needed warming more strongly than the others to achieve a reasonable sublimation rate, and it also seemed that the matrices deposited contained only molecular aggregates and few if any isolated molecules. This could arise because of greater intermolecular forces within these two compounds. Thus despite several attempts, no corresponding azacycloheptatetraenes were observed in the matrix photolyses of **7f** and **14**, only direct formation of the corresponding azepinones. In the case of **7f**, this was evidently not due to any lowered stability of the azacycloheptatetraene, because at least one of the possible intermediates, **10f** or **10g**, was observed in pyrolysis experiments (see below). The available IR data obtained from matrix photolysis of **7f** and **14** are included in Table 2. It is assumed that the most likely azepinone to be formed from **14** would be the isomer **21**, which would arise from nitrene attack at the 6-position in the quinoline ring, rather than **22**, which would arise from nitrene attack at a bridgehead.




**21**




**22**

### Flash vacuum pyrolysis and trapping in matrices

All the azidophenols synthesized were subjected to flash vacuum pyrolysis (FVP) and the products were trapped in $N_2$ at 12–14 K. To achieve this, the azidophenols were sublimed into a stream of the host gas, and the resulting mixture was passed through a quartz tube at 550 °C then deposited as a matrix. Despite several attempts, 5-azido-8-hydroxyquinoline **14** failed to yield identifiable matrix isolated products in these experiments, possibly because of condensation of all the products on cool surfaces near the exit of the hot tube. All the other azidophenols, however, gave product spectra indicating the formation of the same azepinones that had been generated by matrix photolysis. Fig. 3 shows a portion of the IR spectrum recorded after pyrolysis and matrix deposition of **7a** in $N_2$.

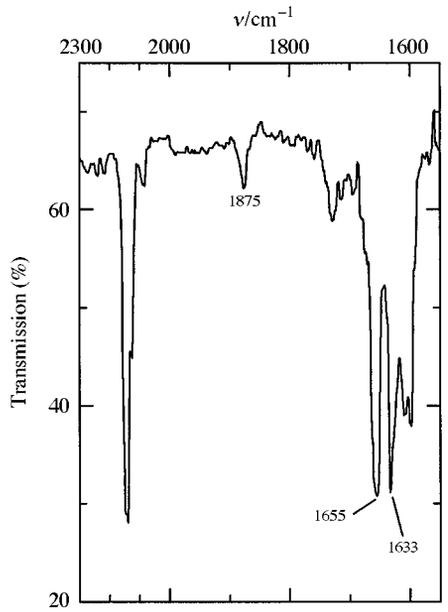



**Fig. 3** IR spectrum in the region 2300–1550 $cm^{-1}$ obtained after vacuum pyrolysis of 4-azidophenol **7a** at 550 °C followed by deposition at 14 K in $N_2$. Note the presence of azide bands near 2100 $cm^{-1}$, belonging to unreacted **7a**, and the *ν*(C=C=N) band of **10a** at 1875 $cm^{-1}$. Note also the similarity of the spectrum to that of Fig. 2(*b*) in the range 1700–1550 $cm^{-1}$.

In the pyrolysis experiments, matrices tended to be of lower optical quality than those in the photolysis experiments, and the IR spectra of the pyrolysates contained numerous weak and broad bands, suggesting the occurrence of further decomposition of the azepinones. Apart from this, the IR spectra of the azepinones obtained from pyrolysis were in good agreement with those obtained by photolysis, and this was especially clear in the *ν*(C=O) and *ν*(C=N) region (bands within 10 $cm^{-1}$).

With two of the azidophenols, 4-azidophenol **7a** and 4-azido-2-nitrophenol **7f**, the matrix IR spectra of the pyrolysates also contained the characteristic *ν*(C=C=N) bands of the corresponding azacycloheptatetraenes **10a** (1875 $cm^{-1}$) (Fig. 3) and **10f** or **10g** (1873 $cm^{-1}$), respectively. Interestingly, the azacycloheptatraene from 4-azido-2-nitrophenol had not been seen in the photolysis experiments. We found no way of altering the pyrolysis and deposition conditions so as to yield detectable amounts of the azacycloheptatetraenes with the other azidophenols.

### Preparative scale photolyses and pyrolyses

From the outset of this work, a major goal was to exploit the low-temperature photochemistry or vacuum pyrolysis of azidophenols on a preparative scale (50 mg or more). It was hoped that at least some examples would be stable at room temperature, once they had been generated in matrices and then warmed up. Several types of preparative scale experiments have thus been carried out: (*i*) conventional solution-phase photolysis at temperatures near to ambient; (*ii*) photolysis of films of neat azidophenols and azidophenols in $CO_2$ matrices at 77 K; (*iii*) FVP in conventional equipment with no carrier gas and with condensation of the pyrolysate at 77 K; (*iv*) photolysis in $N_2$ matrices at 15–30 K; and (*v*) FVP with $N_2$ as the carrier gas, followed by deposition of the pyrolysate mixture as a mat-

rix at 15–30 K. In none of these experiments have we isolated a stable azepinone at room temperature.

Both the parent azidophenol **7a** and the 2,6-dichloro derivative **7c** were photolysed in MeOH, THF–MeOH and other solvents at temperatures in the range −15 to +20 °C, but only intractable tarry or polymeric products were obtained. The same two azidophenols were also photolysed at 77 K, either as neat films or in solid $CO_2$ matrices.[33] In some of these reactions, very dark grey or purplish powders were obtained as products, but these were insoluble in all solvents tested and appeared to be polymeric from mass-spectral analysis. Conventional FVP experiments were carried out with the two dihalo compounds, **7b** and **7c**. The starting materials were sublimed through a furnace at 450–600 °C without a carrier gas, and the pyrolysates were condensed on a cold finger at 77 K. Yellow or orange films of products were obtained, but these proved to be insoluble and therefore were most likely polymeric.

One of the cold cells employed for the matrix work was modified with a large stainless steel vacuum chamber, and the standard cold window was replaced with a copper plate about 10 cm square. Matrices could be deposited on this plate in layers, with photolysis of each layer in sequence. Quantities of up to approximately 250 mg of azidophenols (with an unknown excess of $N_2$) have been deposited and photolysed in this way. The achievable thickness of the matrices is limited by the tendency for the matrix temperature to increase as more and more material is deposited. Beyond about 30 K, evaporation of the matrix host becomes intolerably rapid. After photolysis at low temperature and warming the resulting matrix to room temperature, volatile products can be trapped in a side-arm cooled by liquid $N_2$. Involatile products remain on the copper plate, which can be rotated into a horizontal position, and can be removed by spatula after admission of the atmosphere. The design, construction and operation of this preparative cold cell has been described previously,[34] and it has been used successfully to prepare stable photochemical products, such as phenyl isocyanate from benzoyl azide, in acceptable yields.[35] Photochemical reactions carried out with this modified cold cell are monitored by diffuse reflectance FTIR spectroscopy (DRIFTS).[34]

Three of the azidophenols have been photolysed in the preparative scale cold cell, both as neat films and in $N_2$ matrices: **7b**, **7c** and **7d**. Fig. 4 shows DRIFT spectra taken in a typical experiment with **7c**. About 50 mg of the azidophenol was deposited with an excess of $N_2$ in three layers, and each layer was photolysed until diminution of the strong azide bands near 2100 $cm^{-1}$ showed that photolysis was virtually complete. The residual azide apparent in Fig. 4(*a*) was a small proportion of the total deposited. At this stage, as Fig. 4(*a*) shows, the matrix contained residual starting material, the azacycloheptatetraene **10c** and the azepinone **11c**. The agreement in band positions with the more conventional matrix experiments was good (<10 $cm^{-1}$). Fig. 4(*b*) shows the DRIFT spectrum of the same matrix after warming to room temperature under vacuum overnight. At this stage all the host gas had evaporated. There were also significant changes in the IR spectrum: specifically a decrease, rather than an increase, in absorbance of the azepinone $\nu$(C=O) band at 1683 $cm^{-1}$, growth of a higher frequency $\nu$(C=O) band at 1697 $cm^{-1}$, suggesting loss of conjugation, and growth of numerous other bands in the region 1700–1600 $cm^{-1}$. The changes in the IR spectrum indicate that a chemical reaction had taken place at some point in the warming process. The product turned out to be a dark grey polymeric powder, and was clearly very involatile, since it remained on the copper plate for several hours at room temperature under a vacuum of about $10^{-4}$ mbar. Indeed, the polymer appeared to trap the residual starting material, which would otherwise have evaporated readily. In no such experiments have we succeeded in trapping out more than minute amounts of volatile products.

The modified cold cell was finally used in a series of pyrolysis experiments, in which azidophenols were sublimed into a stream of $N_2$, passed through a hot tube at 550 °C, and the resulting mixtures deposited as matrices. As with all the other preparative scale experiments, the results were uniformly negative.

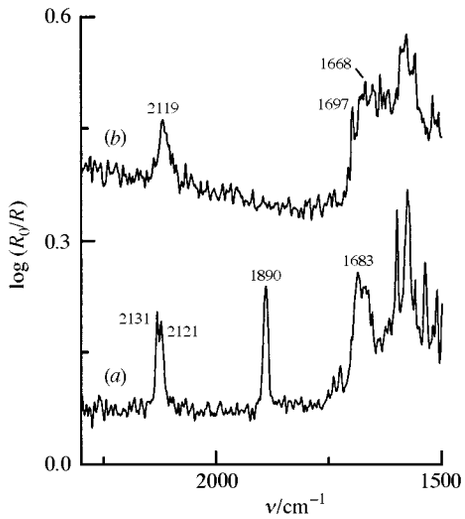



**Fig. 4** DRIFT spectra in the region 2300–1500 $cm^{-1}$ recorded during a preparative scale low-temperature photolysis of 4-azido-2,6-dichlorophenol **7c** in an $N_2$ matrix: (*a*) after deposition of three layers at 18–29 K, with photolysis of the layers ($\lambda$ > 200 nm) for 44 min, 135 min and 120 min, respectively; (*b*) after warming to room temperature under vacuum overnight. It is estimated that about 50 mg of **7c** was deposited in all. The matrix formed upon photolysis contained residual **7c** [$\nu_a(N_3)$ 2131 and 2121 $cm^{-1}$], azacycloheptatetraene **10c** [$\nu$(C=C=N) 1890 $cm^{-1}$] and azepinone **11c** [$\nu$(C=O) 1683 $cm^{-1}$]. Note the retention of **7c** (2119 $cm^{-1}$) even at room temperature.

## Conclusions

We have explored the photochemistry and vacuum pyrolysis of six 4-azidophenols in an attempt to establish a viable preparative route to hitherto elusive 4*H*-azepin-4-ones. Only two 4-azidophenols were reported previously, and one of these, the parent compound **7a**, had been obtained only in an impure form as a liquid at room temperature. We established improved preparative routes for 4-azidophenols, obtained **7a** as a crystalline, though unstable solid, and prepared five other derivatives. The thermal stability of these azidophenols is apparently increased by electron-withdrawing substituents and decreased by electron-releasing substituents.

Matrix isolation experiments showed that all six azidophenols prepared gave the expected azepinones on photolysis at low temperature. FVP followed by trapping in $N_2$ also gave the same set of matrix isolated azepinones. In all but one case, an intermediate hydroxyazacycloheptatetraene was also observed. The identification of the products as azepin-4-ones from a few IR bands, particularly $\nu$(C=O) bands at 1676–1652 $cm^{-1}$, is based on expectations from earlier work on aryl azide photolysis in matrices, the dependence of azepinone formation on the matrix concentration, and the agreement with IR data from the few previously reported azepin-4-ones. The ring expansion of 4-azidophenols *via* hydroxyarylnitrenes and hydroxyazacycloheptatetraenes seems to be reasonably general, and this provides further support for the identification of the azepinones.

Numerous attempts to exploit these reactions preparatively have failed. Photolysis at near ambient temperatures, at 77 K and at 15–30 K produced only polymeric products, once these had been isolated at room temperature, even though it was clear that the desired azepinones had been formed at very low temperatures. Similar attempts to isolate stable azepinones from vacuum pyrolysis experiments were equally unsuccessful.

It is concluded that most 4*H*-azepin-4-ones are intrinsically

unstable—at least those prepared in this work—and that they readily polymerize at room temperature or below. The chemical nature of the polymers formed has not been determined. The previously reported azepin-4-ones seem therefore to be special cases, as was suspected from the paucity of their numbers and the low yields in which they were generally obtained. It is possible that further research may uncover more stable examples, especially if they incorporate extended benzannelation, but it is difficult to think of milder conditions for their work-up and isolation than those we have adopted: sub-ambient temperatures, exclusion of air, and avoidance of all liquids, protic or non-protic.

## Experimental

### General

Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. Routine and matrix transmission IR spectra were recorded on a Perkin-Elmer model 684 spectrometer, with presample chopping, which was interfaced with a Perkin-Elmer 3600 Data Station. $^1$H NMR spectra were recorded at 250.13 MHz on a Bruker WM 250 spectrometer, with $CDCl_3$ as solvent and $Me_4Si$ as internal standard. *J* Values are given in Hz. Microanalyses were carried out by the Microanalytical Service within the Department of Chemistry at Strathclyde University, using a Perkin-Elmer model 2400 Series II analyser. Preparative scale photolyses at ambient temperature were carried out in a Rayonet RPR-208 photochemical reactor with RUL-3000Å (300 nm) lamps or in small annular Pyrex reactors with a central Philips HPK 125 W medium pressure Hg arc, which have been described previously.[36]

In the following descriptions of preparative procedures, the term *isolation with ether* implies extraction of the aqueous phase with several portions of $Et_2O$, washing the combined extracts several times with water, drying over $Na_2SO_4$ or $MgSO_4$, and final removal of the solvent on a rotary evaporator.

### Materials

Nearly all the starting materials and reagents used were commercially available; the exception, 2-nitrophenyl tosylate **20**, was prepared from the phenol by a standard method.[37] Light petroleum for recrystallizations and chromatographic solvents were redistilled before use. Research grade nitrogen (min. 99.995%), used as the matrix host gas, was obtained from BOC Ltd.

### 4-Azidophenol 7a from 4-aminophenol[29]

4-Aminophenol hydrochloride (6.00 g, 41.2 mmol) was dissolved in concentrated hydrochloric acid (1 cm$^3$) and water (20 cm$^3$), and the solution was cooled in an ice bath. A cold solution of sodium nitrite (3.45 g, 50.0 mmol) in water (30 cm$^3$) was then added dropwise with stirring. After the addition was complete, the reaction mixture was stirred for 15 min, then treated dropwise with sodium azide (3.48 g, 53.5 mmol) in water (40 cm$^3$). The resulting solution was left to stir for a further 1.5 h with ice cooling, then allowed to warm to room temperature in the dark overnight. Isolation with ether gave a dark brown solid, which was recrystallized from light petroleum (bp 30–40 °C), affording **7a** as light brown crystals (1.95 g, 35%), mp 40–42 °C (lit.,[29] *ca.* 20 °C); $\nu_{max}$(liq. paraffin mull)/cm$^{-1}$ 3300 (OH), 2210 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 6.92 (2H, d, *J* 9, 3,5-H), 6.83 (2H, d, *J* 9, 2,6-H), 5.13 (1H, br s, OH). Samples of similar purity could be obtained by chromatography on silica, eluting with diethyl ether. The compound decomposed at an appreciable rate at room temperature, and satisfactory elemental analyses could not be obtained, despite several attempts.

### 4-Azido-2,6-dibromophenol 7b

4-Amino-2,6-dibromophenol (5.00 g, 18.7 mmol) was dissolved in a solution of acetic acid (40 cm$^3$), water (20 cm$^3$) and concentrated hydrochloric acid (10 cm$^3$). The solution was cooled to −3 °C in an ice–salt bath, and sodium nitrite (2.00 g, 28.9 mmol) in water (16 cm$^3$) was added dropwise with stirring over 10 min. The reaction mixture was stirred at −3 °C for 15 min and was then treated with sodium azide (2.3 g, 28.3 mmol) in water (20 cm$^3$), added over 10 min. The resultant mixture was stirred at 0 °C for a further 1 h, and was then allowed to warm to room temperature overnight in the dark. Isolation with ether gave a dark brown solid, which was recrystallized from light petroleum (bp 30–40 °C), to give **7b** as light brown crystals (2.3 g, 40%), mp 76–78 °C (decomp.) (Found: C, 24.6; H, 1.0; Br, 54.5; N, 14.0. $C_6H_3Br_2N_3O$ requires C, 24.6; H, 1.0; Br, 54.6; N, 14.3%); $\nu_{max}$(liq. paraffin mull)/cm$^{-1}$ 3370 (OH), 2123 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 7.15 (2H, s, 3, 5-H), 5.79 (1H, br s, OH).

### 4-Azido-2,6-dichlorophenol 7c

4-Amino-2,6-dichlorophenol (2.00 g, 11.2 mmol) was partially dissolved in a solution of acetic acid (20 cm$^3$), concentrated hydrochloric acid (5 cm$^3$) and water (20 cm$^3$) at room temperature. The resulting mixture was cooled in an ice bath, then sodium nitrite (0.85 g, 12.3 mmol) in water (8.5 cm$^3$) was added dropwise. The reaction mixture was stirred for 15 min, then treated dropwise with sodium azide (0.80 g, 12.3 mmol) in water (8 cm$^3$), stirred with cooling for a further 1 h, and then allowed to warm to room temperature overnight in the dark. Isolation with ether gave a dark solid, which was recrystallized from light petroleum (bp 30–40 °C), followed by vacuum sublimation at ambient temperature and *ca.* 0.1 mbar, to yield **7c** as whitish needles (1.83 g, 80%), mp 71–72 °C (decomp.) (Found: C, 35.2; H, 1.4; N, 20.6; Cl, 34.7. $C_6H_3Cl_2N_3O$ requires C, 35.3; H, 1.5; N, 20.6; Cl, 34.8%); $\nu_{max}$(liq. paraffin mull)/cm$^{-1}$ 3370 (OH), 2123 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 6.97 (2H, s, 3,4-H), 5.80 (1H, br s, OH).

### 4-Azido-2-chloro-6-methylphenol 7d

4-Amino-2-chloro-6-methylphenol (2.50 g, 17.6 mmol) was partially dissolved in a solution of acetic acid (25 cm$^3$), concentrated hydrochloric acid (5 cm$^3$) and water (20 cm$^3$). The mixture was stirred at room temperature for approximately 10 min, cooled in an ice–salt bath to −3 °C, and sodium nitrite (1.50 g, 21.7 mmol) in water (15 cm$^3$) was added dropwise during 20 min. The resulting solution was then treated dropwise with sodium azide (1.80 g, 27.7 mmol) in water (18 cm$^3$), stirred for a further 1.5 h, and then left to warm to room temperature overnight in the dark. Isolation with ether gave a dark grey solid, which was recrystallized from light petroleum (bp 30–40 °C), giving **7d** as light grey crystals (1.30 g, 44%), mp 42–44 °C; $\nu_{max}$(liq. paraffin mull)/cm$^{-1}$ 3331 (OH), 2117 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 6.85 (1H, d, *J* 2.5, 3-H), 6.74 (1H, m, 5-H), 5.57 (1H, br s, OH), 2.28 (3H, s, $CH_3$). The compound decomposed too rapidly at room temperature for satisfactory elemental analysis, despite several attempts.

### 4-Azido-2-nitrophenol 7f[29]

4-Amino-2-nitrophenol (3.00 g, 19.5 mmol) was dissolved in a solution of acetic acid (30 cm$^3$), concentrated hydrochloric acid (15 cm$^3$) and water (30 cm$^3$). The solution was stirred at room temperature for approximately 10 min, cooled in an ice–salt bath to −3 °C, and treated dropwise during 7 min with sodium nitrite (1.80 g, 26.1 mmol) in water (18 cm$^3$). The mixture was stirred at −3 °C for a further 20 min, then sodium azide (2.00 g, 29.00 mmol) in water (20 cm$^3$) was added dropwise. The resulting mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature overnight in the dark. Isolation with ether gave dark yellow crystals, which were recrystallized from light petroleum (bp 30–40 °C), followed by vacuum sublimation at *ca.* 0.1 mbar, to give **7f** as light yellow crystals (2.25 g, 64%), mp 80–82 °C (lit.,[29] 91 °C) (Found: C, 40.2; H, 2.0; N, 31.0.

$C_6H_4N_4O_3$ requires C, 40.0; H, 2.2; N, 31.1%); $\nu_{max}$(liq. paraffin mull)/$cm^{-1}$ 3235 (OH), 2122 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 10.42 (1H, s, OH), 7.75 (1H, s, 3-H), 7.26 (1H, d, *J* 9, 5-H), 7.18 (1H, d, *J* 9, 6-H).

### 5-Azido-8-hydroxyquinoline 14

5-Amino-8-hydroxyquinoline dihydrochloride (1.00 g, 4.2 mmol) was dissolved in a solution of concentrated hydrochloric acid (0.4 $cm^3$) and water (5 $cm^3$), cooled to −3 °C in a salt–ice bath, stirred for 10 min, then treated dropwise with a cold solution of sodium nitrite (0.50 g, 7.2 mmol) in water (5 $cm^3$). The mixture was stirred for 20 min, then treated dropwise with sodium azide (0.60 g, 9.2 mmol) in water (40 $cm^3$), stirred at 0 °C for a further 1.5 h, then allowed to warm to room temperature over 24 h in the dark. Isolation with ether gave a dark brown solid, which was recrystallized from light petroleum (bp 30–40 °C) to yield **14** as light brown crystals (0.36 g, 32%), mp 117–119 °C (Found: C, 58.2; H, 3.0; N, 30.0. $C_9H_6N_4O$ requires C, 58.0; H, 3.2; N, 30.1%); $\nu_{max}$(liq. paraffin mull)/$cm^{-1}$ 2298 (OH), 2213 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 8.83 (1H, dd, *J* 4, 1.5, 2-H), 8.40 (1H, dd, *J* 8, 1.5, 4-H), 8.11 (1H, br s, OH), 7.47 (1H, dd, *J* 8, 4, 3-H), 7.24 (1H, d, *J* 8, 6-H), 7.18 (1H, d, *J* 8, 7-H).

### 4-Aminophenyl tosylate 18[38,39]

**From 17.** 4-Aminophenol **17** (2.6 g, 23 mmol) was partially dissolved in dichloromethane (70 $cm^3$), and the mixture was treated dropwise with stirring at room temperature with a solution of toluene-4-sulfonyl chloride (4.53 g, 23.7 mmol) and triethylamine (4.4 g, 43 mmol) in dichloromethane (30 $cm^3$). After stirring for a further 30 min, the resulting solution was washed with dilute aq. NaOH then water, dried ($MgSO_4$) and evaporated, to give a cream-coloured solid, which was recrystallized from ethanol, affording **18** as white crystals (4.4 g, 70%), mp 140–141 °C (lit.,[38,39] 142.5 °C).

**From 20.** 4-Nitrophenyl tosylate **20** (2.93 g, 10 mmol) was boiled for 2 h in a suspension of stannous chloride dihydrate (6.77 g, 30 mmol) in concentrated hydrochloric acid (14 $cm^3$). After cooling, the solution was neutralized with dilute aq. NaOH, and the product extracted from the resulting suspension with chloroform (3 × 25 $cm^3$). The combined extracts were washed several times with saturated aq. $NaHCO_3$, dried ($MgSO_4$) and evaporated. The solid product was recrystallized from methanol, affording **18** as white crystals (1.91 g, 73%).

### 4-Azidophenyl tosylate 19

4-Aminophenyl tosylate **18** (2.0 g, 7.6 mmol) was dissolved in a solution of acetic acid (45 $cm^3$), concentrated hydrochloric acid (4 $cm^3$) and water (20 $cm^3$) and cooled to 0 °C. Sodium nitrite (0.58 g, 8.9 mmol) in water (5 $cm^3$) was added dropwise with stirring during 5 min. The solution was stirred for a further 5 min, then sodium azide (0.55 g, 8.46 mmol) in water (5 $cm^3$) was added, and the resulting solution stirred for 1 h at 0 °C. Isolation with ether, including one wash with dilute aq. NaOH, gave **19** as a clear oil (1.98 g, 90%), which was not further purified, because of problems with decomposition; $\nu_{max}$(liq. film)/$cm^{-1}$ 2132 and 2103 ($N_3$); $\delta_H$(250 MHz; $CDCl_3$; $Me_4Si$) 7.75 (2H, d, *J* 9), 7.35 (2H, d, *J* 9), 6.98 (4H, m), 2.48 (3H, s, $CH_3$).

### 4-Azidophenol 7a from 19

4-Azidophenyl tosylate **19** (3.0 g, 10.4 mmol) was added to a solution of potassium hydroxide (6.75 g, 0.12 mol) in water (110 $cm^3$) and ethanol (110 $cm^3$), and the resulting solution was warmed for 1 h at 35–40 °C. The solution was cooled and neutralized with acetic acid. Isolation with ether gave **7a** (1.33 g, 95%).

### Matrix-isolation equipment and matrix experiments

Standard, small scale matrix experiments were carried out in two low-temperature cells, both of which have been described previously.[40,41] The first was based on an Air Products Displex model CSA-202 closed-cycle helium refrigerator, and was equipped with a glass and metal vacuum shroud; the second utilized a more recent APD Cryogenics Displex model HC-2 refrigerator, equipped with a stainless steel shroud. Both shrouds were fitted with external KBr windows, and were pumped to about $10^{-5}$ mbar† by means of Edwards Diffstak model 63-105M oil diffusion pumps. Matrices were deposited on CsBr cold windows in nickel-plated copper holders. Temperatures were measured on the cold window holders with Chromel-Au-0.07 atom-% Fe thermocouples, and could be varied by means of small resistance heaters connected to temperature controllers. The base temperatures of the cold cells were 12–14 K. Small secondary vacuum lines were used to handle the matrix gases and control deposition rates *via* fine control needle valves.

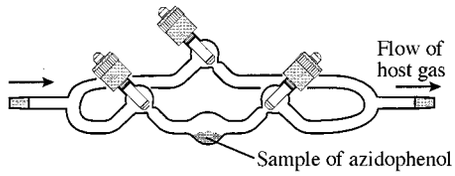



**Fig. 5** Glass side-arm fitted with PTFE valves with integral O-rings and standard ground-glass cones at each end. The host gas can be passed directly over the sample, which increases the sublimation rate, or sublimation can take place from one branch, with the host gas passing along the other.

Matrices were deposited by sublimation of the azidophenol contained in a glass side-arm (Fig. 5) attached to the vacuum chamber of the cold cell, while a stream of $N_2$ host gas was passed over the sample. The rate of flow of the host gas was controlled by a fine needle valve and the azidophenol sample could be warmed with a heat gun if necessary. The progress of deposition was monitored by IR spectroscopy.

Photolyses were carried out with an Oriel 200 W high pressure Hg arc. For full arc irradiation ($\lambda$ > 200 nm), light from this lamp was roughly collimated with a quartz lens and, to remove IR radiation, was then passed through a water filter (13 cm pathlength) fitted with quartz windows. Alternatively the beam was focused on the entrance slits of an Applied Photophysics high radiance *f*/3.4 monochromator. In the earlier experiments it was found that monochromatic light did not lead to significantly more selective photolyses, so in most experiments full arc irradiation was employed to minimize irradiation times.

Pyrolysis experiments made use of a specially designed heated tube in a water-jacketed vacuum chamber (Fig. 6), which was mounted on the vacuum shroud of the cold cell. Heating was achieved by tungsten or nichrome coils around the tube, supplied from appropriate AC power sources *via* water-cooled terminals. Temperatures of up to about 600 °C could be attained, which were measured by a K type thermocouple attached to the midpoint of the outside of the hot tube with fireproof cement.

Preparative scale matrix experiments (up to two or three hundred mg) were carried out in one of the cold cells, with a cooled copper plate about 10 cm square replacing the standard cold window, enclosed in a large stainless steel vacuum shroud. Reactions were monitored by diffuse reflectance IR spectroscopy with a specially modified Bomem MB-100 FTIR spectrometer interfaced, *via* a DSP-100 fast Fourier transform card, with a Viglen 25 MHz 386SX computer with a co-processor. Both DTGS and MCT detectors were available. Photolyses were performed with the aid of a fused silica plano-concave lens (50 mm diameter, 100 mm focal length), in order to illuminate the cold plate as evenly as possible. Volatile products could be recovered by warming the cold plate and condensation in a

† 1 bar = $10^5$ Pa.

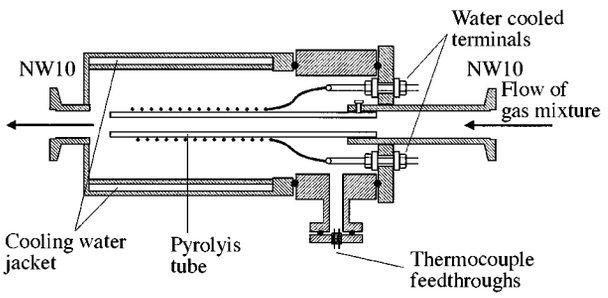



**Fig. 6** Section through the water-cooled vacuum pyrolysis furnace used for matrix FVP experiments. The main body components were made of brass and copper, and were joined together with single O-ring seals. The furnace was coupled to the cold cell and gas line *via* NW10 flanges and appropriate seals.

glass trap attached to the vacuum shroud and cooled by liquid nitrogen. The design, construction and operation of this set-up have been described in detail previously.[34] Spectra were acquired either with the supplied Bomem software or with Galactic Industries LabCalc. A reflection spectrum from the cold plate before sample deposition was taken as a reference in each experiment.

At an early stage of the project, low-temperature preparative scale photolyses of **7c** as a neat solid or in $CO_2$ matrices were carried out at 77 K, on the surface of a brass drum cooled by liquid nitrogen and enclosed in a glass vacuum shroud.[33] Additional preparative scale pyrolyses at 450–600 °C were carried out at Edinburgh University on conventional FVP equipment, without carrier gas. In these experiments the pyrolysate was condensed on a glass cold finger at 77 K.

## Acknowledgements

We thank Dr H. McNab for use of flash vacuum pyrolysis equipment at Edinburgh University and for assisting in the experiments, Dr R. Withnall and Professor L. Andrews for advice and help in the construction of the pyrolysis equipment used in the matrix FVP experiments, and Dr G. R. Proctor for helpful discussions. We gratefully acknowledge support from the EPSRC (equipment grants to I. R. D. and a studentship to S. L. G.), from the Royal Society (equipment grant to I. R. D.), and from the Libyan Arab Jamahria Government for a studentship (A. A. E. A.).

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*Paper* 7/01595J
*Received* 6*th March* 1997
*Accepted* 14*th April* 1997