

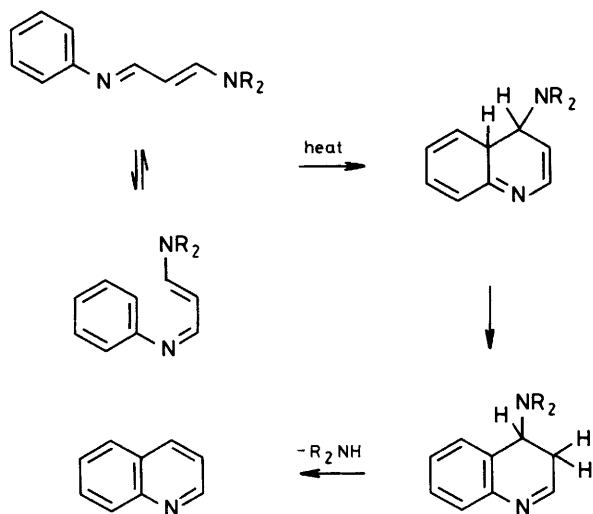
## Thermolysis of Polyazapentadienes. Part 10.<sup>1,2</sup> Flash Vacuum Pyrolysis of Azoalkenes and Some Azocarbonyl Compounds

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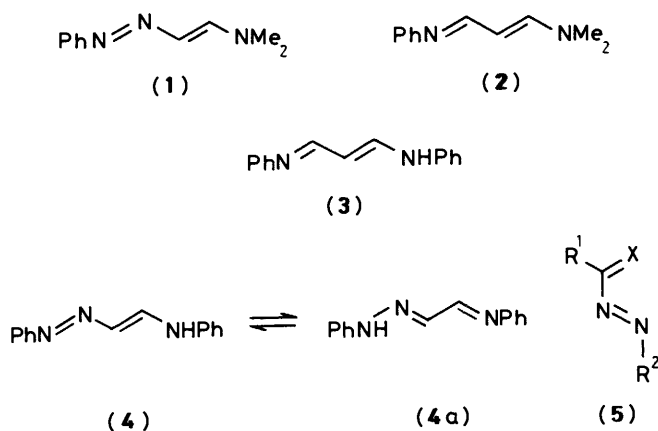
Thermolysis of the azoalkenes (1) and (6)—(8) takes place by 4 $\pi$ -electron electrocyclicisation, followed by elimination of HCN to give imines. Decomposition of the related compounds (9)—(12) is less well defined, though the indole (22) has been identified from the thermolysis of (10) at high temperature. Alternatively, the azo ketones (15)—(18) undergo homolysis of the central C—N bond at 750 °C, and low yields of biaryls, formed by intermolecular radical coupling are generally found. Decarbonylation of intermediate aroyl radicals is extremely rapid under these conditions.

The work described in this, and in the following paper<sup>3</sup> has its origins in an attempt to extend the 'electrocyclic ring closure with elimination' sequence<sup>4</sup> (Scheme 1) to the readily available



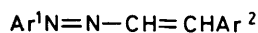
Scheme 1.

azo compound<sup>5,6</sup> (1), as a possible source of the cinnoline ring system. However, our previous work on gas phase reactions of related systems had shown that: (a) quinoline was only a minor product from (2) owing to competing hydrogen transfer processes;<sup>7</sup> (b) though quinoline is obtained in good yield from the diaryl compound (3),<sup>8</sup> the corresponding triaza derivative (4) exists in the hydrazone tautomer (4a) and gives quinoxaline,

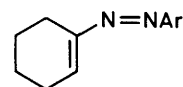


by a free radical mechanism, on pyrolysis.<sup>9</sup> In addition, (1), being an azo compound, might be expected to extrude N<sub>2</sub> under pyrolytic conditions. In fact, *none* of these events took place when (1) was pyrolysed, and instead HCN was eliminated, by formal cleavage of the two double bonds of the triazapentadiene chain.<sup>2</sup> At the time of the preliminary communication,<sup>2</sup> such behaviour of non-cyclic azo compounds was unprecedented,<sup>10</sup> though similar reactions had been observed for 2-aza dienes<sup>11</sup> and some heteroanalogues.<sup>12</sup> In this paper, we give full details of the pyrolysis of the model compound (1), and of the extension of the work to systems of general formula (5), including simple azo alkenes<sup>13</sup> (5; X = R<sub>2</sub>C) and azo carbonyl compounds<sup>14</sup> (5; X = O).

The selection of compounds (5) for pyrolysis was dictated in part by constraints from the literature:<sup>13</sup> C-alkylphenyl-azoalkenes, for example, are not suitable, because they decompose even at -20 °C.<sup>15</sup> However, the C-aryl derivatives (6) and (7) are readily obtainable,<sup>16</sup> and the *p*-chlorophenyl compound (8) was made by the same method. Similarly, the arylazocyclohexenes<sup>17</sup> (9) and (10) and the esters<sup>18</sup> (11) and (12) are well characterised and stable at room temperature. Unfortunately, attempts to prepare C-substituted dimethylamino-azo alkenes analogous to (1) by condensation of amines with the carbonyl derivatives (13) and (14) (*cf.* ref. 5) were unsuccessful.



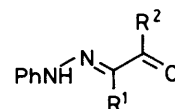
- (6) Ar<sup>1</sup> = Ar<sup>2</sup> = Ph  
 (7) Ar<sup>1</sup> = *o*-ClC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph  
 (8) Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>



- (9) Ar = Ph  
 (10) Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>

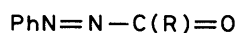


- (11) R = Me  
 (12) R = Et



- (13) R<sup>1</sup> = Me, R<sup>2</sup> = H  
 (14) R<sup>1</sup> = H, R<sup>2</sup> = Me

Azo ketones have been made<sup>19</sup> by oxidation of the corresponding hydrazide using potassium ferricyanide in a two-phase system using 2,4,6-tri(4-*t*-butylphenyl)phenol as phase transfer catalyst. We had difficulties in separating analogous catalysts from the final product, and found that the oxidation proceeded satisfactorily in up to 86% yield, in complete *absence* of catalyst, to give the ketones (15)—(18) as red oils. In their mass spectra



(15) R = Ph

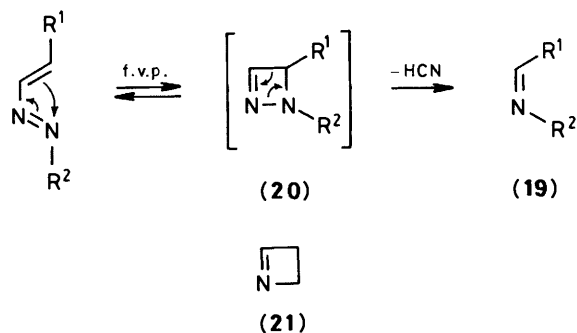
(16) R = *p*-MeC<sub>6</sub>H<sub>4</sub>(17) R = *o*-MeOC<sub>6</sub>H<sub>4</sub>

(18) R = Me

the molecular ion was not normally observable, though significant ( $M + 2$ ) peaks were always obtained.

With the exception of (1), which has a unique breakdown pattern,<sup>6</sup> the mass spectra of the other compounds studied all show cleavage of the bond adjacent to the azo function [or its equivalent in the cases of (15)–(18)] as the dominant pathway though either or both of the resulting fragments may appear in the spectrum. Thus the aryl cation ( $\text{Ar}^+\text{CO}$ ) gives rise to the base peak in the spectra of (15)–(17) [e.g. (16;  $m/z$  119)], while the phenylazo cation ( $m/z$  105) is found *en route* to the base peak ( $\text{Ph}^+$ ) in the spectra of (11), (12), and (18). Evidence for both fragments is obtained from the spectra of the azoalkenes (6)–(10), in which the base peak ( $\text{Ar}^+$ ) is formed from the arylazo cation [e.g. (8),  $m/z$  105 (9) and 77 (100)] though the alkenyl cation ( $\text{ArCH} = \text{CH}^+$ ) is also present [e.g. (8),  $m/z$  139, 137 (14, 42) and (9)  $m/z$  81 (60)].

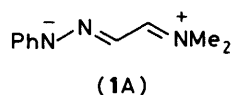
Flash vacuum pyrolysis of the azo alkene (1) at 650 °C ( $2 \times 10^{-3}$  Torr) gave a 41% yield of *N,N*-dimethyl-*N'*-phenylformamidine (19; R<sup>1</sup> = NMe<sub>2</sub>, R<sup>2</sup> = Ph), as the only significant product, by formal elimination of HCN from the starting material. This surprising cleavage of two double bonds in the substrate is best explained by a two-step mechanism (Scheme 2) in which a 4π-electron electrocyclic ring closure



Scheme 2.

gives an intermediate diazetine (20) which can collapse to the observed product. There is precedence for the second step in the thermal behaviour of fused diazetines<sup>20</sup> and for the overall sequence in the behaviour of 2-aza dienes;<sup>11</sup> the reverse of the first step in this case (*viz* electrocyclic ring opening of an azetine) has been observed in the flash vacuum pyrolysis (f.v.p.) of the parent compound (21) under relatively mild conditions (450 °C).<sup>21</sup>

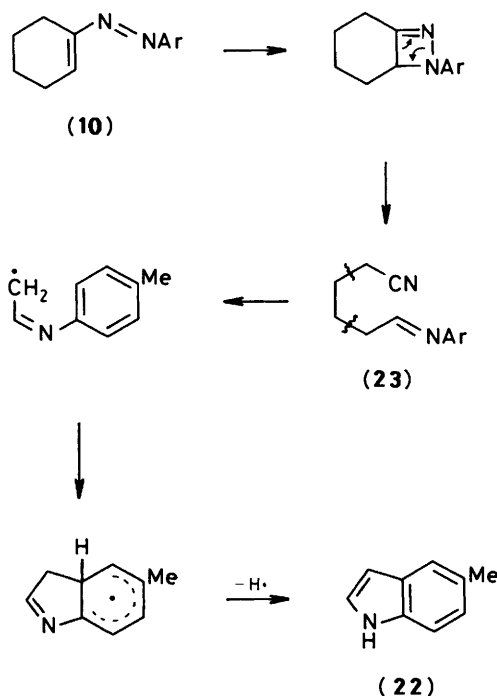
In the present example, the polarity of the conjugated system caused by the electron donating dimethylamino group [resonance form (1A)] is an unknown influence on the position



of the equilibrium which is the first step of Scheme 2 (see also the following paper). However, pyrolysis of the diaryl derivative (6) under the same conditions gave *N*-benzylideneaniline (19; R<sup>1</sup> = R<sup>2</sup> = Ph) in 59% yield, and even incorporation of the mildly

electron withdrawing *p*-chlorophenyl substituent in (8) gave the corresponding product (19; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Ph) (48%). Similarly, modification of the aryl group on the azo function had little effect on the course of the reaction, and *N*-benzylidene-*o*-chloroaniline (19; R<sup>1</sup> = Ph, R<sup>2</sup> = *o*-ClC<sub>6</sub>H<sub>4</sub>) (14%) was obtained from (7). The quoted yields in the last two cases are not strictly comparable, since the normal pyrolysis method could not be used owing to decomposition of the substrates below their sublimation temperature. Instead, the solid starting materials were dropped down a vertical furnace tube *in vacuo*,<sup>22</sup> though these conditions are not ideal for unimolecular reactions. Nevertheless, the isolation of a single benzylideneaniline derivative in both cases is consistent with the intramolecular mechanism *via* the diazetine (Scheme 2).

In the context of these results, the pyrolyses of the remaining azoalkenes (9)–(12) were disappointing. Though the red cyclohexene derivatives (9) and (10) were converted, at a slightly slower furnace temperature (600 °C) into colourless pyrolysates, only aniline, and *p*-toluidine respectively could be detected by gas chromatography/mass spectrometry (g.c.-m.s.). The pressure remained steady throughout the reactions, which confirms that N<sub>2</sub> is not formed to any extent. A detailed study of the pyrolysis of the methyl labelled derivative (10) by <sup>1</sup>H n.m.r. spectroscopy showed at least nine methyl singlets in the region δ<sub>H</sub> 2.20–2.35, while the mass spectrum of the crude non-basic components only indicated the presence of oligomers ( $m/z$  386, 385) which were not identified. At higher temperatures (e.g. 850 °C), the reaction was much cleaner, and two products were formed, which were identified as *p*-toluidine (*ca.* 28%) and 5-methylindole (22; *ca.* 21%) by g.l.c. and <sup>1</sup>H n.m.r. spectroscopy, (though the relative yields were somewhat variable). Since the *p*-tolyl ring appears in both products, they must arise by competitive processes. The formation of the *p*-toluidine may be initiated by tautomerisation to a hydrazone, followed by free radical cleavage,<sup>9</sup> but the degradation of the cyclohexene unit to generate C-2 and C-3 of the indole (22) is most unusual. One possible route involves radical cleavage of the imino nitrile (23) (formed by the mechanism of Scheme 2) followed by cyclisation (Scheme 3). It is known that hydrocarbon chains can begin to

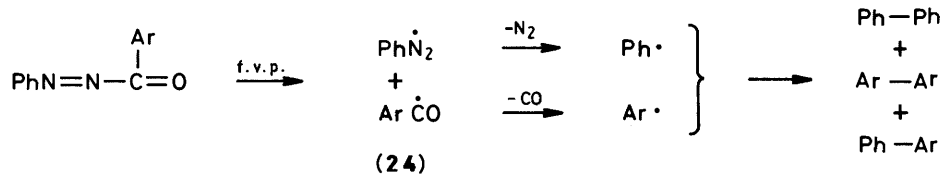


Scheme 3.

degrade at temperatures above 500 °C under f.v.p. conditions,<sup>23</sup> and the resonance stability of the species formed will also provide a driving force in the present example.

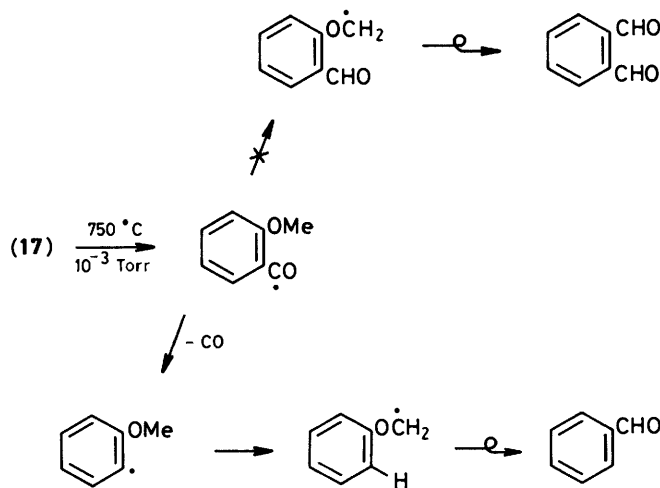
The incorporation of a strong electron-withdrawing group as in (11) and (12) also totally disrupts the thermal chemistry of the azo alkene unit. In these cases, no clear pattern emerged, with traces of aniline being obtained *via* an unknown mechanism as the only consistent product.

In the pyrolyses of the azocarbonyl compounds (15)–(18), the presence of a substituent on the carbon adjacent to the azo function provides a monitor for the operation of the electrocyclic-elimination mechanism (Scheme 2) since the corresponding nitrile would be easily identified by gas chromatography. In the event, these substrates required a higher temperature (750 °C) for conversion into products, and at most only traces of nitriles were formed. The major products at 750 °C were biaryls, (10–20%) which suggests that an alternative mechanism is taking place to generate free radicals (Scheme 4). The intermolecular nature of the coupling was demonstrated by the pyrolysis of (16) (Scheme 4, Ar = *p*-tolyl),



Scheme 4.

in which all three cross-over products were identified by g.c.-m.s. Though the yields of biaryls were low (10–20%), this seems to be a characteristic of the generation of aryl radicals under f.v.p. conditions,<sup>24</sup> and, in addition, quantities of the monomeric aromatic hydrocarbons were collected which are presumably formed from the aryl radicals by high-energy hydrogen-abstraction processes. No benzils, and only traces of benzophenones were detected, which suggests that the aroyl radicals (24) lose CO rapidly at 750 °C, though it is known that coupling products may be obtained under milder conditions.<sup>25</sup> In an attempt to intercept the aroyl radical by intramolecular reaction prior to its decomposition, the *o*-methoxyphenyl derivative (17) was pyrolysed. Methoxy groups are known to be efficient intramolecular traps of both *ortho*-radicals<sup>26</sup> and adjacent phenyl radicals,<sup>27</sup> with the formation of an aldehyde, which can be readily detected (Scheme 5). Only benzaldehyde



Scheme 5.

(28%) was obtained and so decarbonylation must be extremely rapid at 750 °C.

In conclusion, our results, together with the reported case of 2-methyl-3,4-diazapenta-1,3-diene<sup>10</sup> have established that cleavage of HCN, probably *via* the mechanism of Scheme 2, is general for azo alkene thermolysis in the absence of strong electronic perturbation, or other complicating factors. That this behaviour does not extend to azo carbonyl derivatives is perhaps not surprising, though the respective thermolysis temperatures suggest that the electrocyclic-elimination process is positively disfavoured, rather than being circumvented by a lower-energy radical pathway.

## Experimental

<sup>1</sup>H N.m.r. spectra were recorded at 80 or 100 MHz and <sup>13</sup>C spectra were measured at 20 MHz, for solutions in [<sup>2</sup>H]-chloroform. B.p.s generally refer to oven temperatures of a Kugelrohr apparatus.

The following precursors were obtained by literature

methods: 5,5-dimethyl-1-phenyl-1,2,5-triazapentadiene<sup>5,6</sup> (1), m.p. 84–86 °C (lit.,<sup>6</sup> 84–86 °C); 1,4-diphenyl-1,2-diazabutadiene (6) m.p. 113–115 °C (lit.,<sup>16</sup> 111 °C); 1-(*o*-chlorophenyl)-4-phenyl-1,2-diazabutadiene (7) as a semi-solid which decomposed on attempted distillation, *m/z* 244 (*M*<sup>+</sup>, 24%), 243 (36), 242 (80), 241 (76), 141 (4), 139 (12), 113 (17), 111 (52), 105 (56), 103 (100), and 77 (76) [lit., b.p.<sup>16</sup> 160 °C (0.1 Torr)]; 1-phenylazocyclohex-1-ene (9), m.p. 30–33 °C (lit.,<sup>17</sup> 32–34 °C) δ<sub>C</sub> 155.16 (q), 152.72 (q), 141.66, 129.63, 128.73 122.10, 26.26, 22.56, 22.19, and 21.88; 1-*p*-tolylazocyclohex-1-ene (10), m.p. 56–58 °C (lit.,<sup>17</sup> 59 °C), δ<sub>C</sub> 155.03 (q), 150.74 (q), 140.78, 139.94 (q), 129.40, 122.08, 26.23, 22.60, 22.23, 21.94, and 21.19; methyl 3-(phenylazo)but-2-enoate (11) as a red oil, b.p. 88–92 °C (0.1 Torr), which slowly crystallised (lit., m.p.,<sup>18</sup> 46 °C); ethyl 3-(phenylazo)but-2-enoate (12), m.p. 49–50 °C (lit.,<sup>18</sup> 51 °C).

1-Phenyl-4-(*p*-chlorophenyl)-1,2-diazabutadiene (8).—A mixture of formyltriphenylphosphonium phenylhydrazone perchlorate<sup>16</sup> (4.3 g, 9 mmol), *p*-chlorobenzaldehyde (1.26 g, 9 mmol), and triethylamine (1.1 g, 11 mmol) in 1,1-dichloroethane (45 ml) was heated under reflux for 2 h. The solvent was removed under reduced pressure and the residual oil was triturated with toluene. The triethylammonium perchlorate which formed was filtered and the filtrate was concentrated under reduced pressure. Chromatography of the residue on silica gel (with methylene dichloride as eluant) gave the required compound, (29%), m.p. 102–104 °C (Found: C, 69.15; H, 4.6; N, 11.55. C<sub>14</sub>H<sub>11</sub>ClN<sub>2</sub> requires C, 69.3; H, 4.55; N, 11.55%); δ<sub>H</sub> 8.1–7.3 (11 H, m); δ<sub>C</sub> 152.78 (q), 146.70, 140.68, 135.35 (q), 133.36 (q), 130.78, 129.09, 128.94, and 122.59; *m/z* 244 (*M*<sup>+</sup>, 15%) 242 (*M*<sup>+</sup>, 46), 207 (33), 139 (14), 137 (42), 102 (30), 101 (30), and 77 (100).

3-Phenyl-2,3-diazaprop-2-en-1-ones.—The appropriate phenylhydrazide (1 mmol) was dissolved in methylene dichloride (30 ml) and shaken with a saturated solution of potassium ferricyanide in sodium hydroxide (2M; 25 ml). The

organic layer was separated, washed with water (20 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated under reduced pressure. The resulting red oil was then purified by bulb-to-bulb distillation. No parent ion peak was observed in their mass spectra but instead there was a consistent peak at  $m/z$  ( $M + 2$ ). The following compounds were prepared in this way: (a) 1,3-diphenyl-2,3-diazaprop-2-en-1-one (**15**) (86%), m.p. ca. 29 °C, b.p. 128–130 °C (0.2 Torr) (lit.,<sup>19</sup> m.p. 30 °C);  $v_{\text{max}}$  1 710  $\text{cm}^{-1}$  (CO);  $m/z$  212 [ $(M + 2)^+$ , 4%], 182 (6), 105 (100), and 77 (97); (b) 3-phenyl-1-(*p*-tolyl)-2,3-diazaprop-2-en-1-one (**16**) (54%), b.p. 130–133 °C (0.2 Torr) (Found: C, 74.8; H, 5.15; N, 12.45%.  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$  requires C, 75.0; H, 5.4; N, 12.5%);  $v_{\text{max}}$  1 705  $\text{cm}^{-1}$  (CO);  $\delta_{\text{H}}$  8.1–7.3 (9 H, m) and 2.44 (3 H, s);  $\delta_{\text{C}}$  181.49 (q), 151.71 (q), 145.31 (q), 132.89, 130.17, 129.22, 128.95, 127.78 (q), 123.06, and 21.44;  $m/z$  226 [ $(M + 2)^+$ , 3%], 119 (100), 91 (40), and 77 (11); (c) 1-(*o*-methoxyphenyl)-3-phenyl-2,3-diazaprop-2-en-1-one (**17**) (21%), b.p. 162–167 °C (0.2 Torr) (Found: C, 69.9; H, 4.85; N, 11.8.  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$  requires C, 70.0; H, 5.05; N, 11.65%);  $v_{\text{max}}$  1 690  $\text{cm}^{-1}$  (CO);  $\delta_{\text{H}}$  8.1–6.9 (9 H, m) and 3.77 (3 H, s);  $\delta_{\text{C}}$  182.98 (q), 160.08 (q), 152.03 (q), 135.56, 132.55, 132.40, 130.75 (q), 129.02 (2C), 122.99 (2C), 120.54, 112.15, and 55.91;  $m/z$  242 [ $(M + 2)^+$ , 6%], 182 (16), 135 (100), 105 (16), 92 (35), and 77 (98); (d) 1-methyl-3-phenyl-2,3-diazaprop-2-en-1-one (**18**) (19%), b.p. 90–94 °C (0.2 Torr). This compound is quoted in the literature<sup>19</sup> but there are no physical constants available for comparison:  $v_{\text{max}}$  1 750  $\text{cm}^{-1}$  (CO);  $\delta_{\text{H}}$  7.9–7.3 (5 H, m) and 2.42 (3 H, s);  $m/z$  150 [ $(M + 2)^+$ , 14%], 136 (10), 135 (7), 107 (19), 105 (17), 91 (29), and 77 (100).

**Pyrolysis Experiments.**—The majority of the pyrolyses were carried out on a small scale (50–100 mg) using a horizontal furnace tube as previously described,<sup>9</sup> and products were identified by n.m.r., g.l.c. (5% Carbowax 20 M or 5% SE 30) and g.c.-m.s. comparison with authentic samples. Yields were generally estimated by n.m.r. spectroscopy, by the addition to the crude pyrolysate of cyclohexane (5  $\mu\text{l}$ ) as integral calibrant. In some cases, extensive decomposition of the starting material took place in the sublimation inlet, and for these, acceptable results were obtained by dropping the solid, *in vacuo*, down a vertical furnace tube containing a loose plug of silica wool.<sup>22</sup>

Parameters for small-scale pyrolyses are quoted as follows: substrate, inlet temperature (where appropriate), furnace temperature, pressure, pyrolysis time, and products. For pyrolyses using the horizontal furnace, substrate decomposition in the inlet gave a residue of <8% in all cases.

(i) **Azoalkenes.** (a) 5,5-Dimethyl-1-phenyl-1,2,5-triazapentadiene (**1**) (0.054 g, 0.30 mmol); 50 °C; 650 °C,  $2 \times 10^{-3}$  Torr; 90 min; *N,N*-dimethyl-*N'*-phenylformamidine (41%). The <sup>1</sup>H n.m.r. spectrum of the crude pyrolysate showed peaks at  $\delta_{\text{H}}$  7.42 (1 H, s), and 2.90 (6 H, s), corresponding to the methine, and methyl groups respectively of the amidine. (An authentic sample<sup>28</sup> had  $\delta_{\text{H}}$  7.42 and 2.93). Reaction with picric acid in acetone gave the amidinium picrate, m.p. and mixed m.p. 159–162 °C (from methanol) [lit.,<sup>28</sup> 162–164 °C (decomp.)],  $\delta_{\text{H}}$  8.69 (1 H, s), 8.55 (2 H, s), 7.40 (5 H, s), 3.35 (3 H, s), and 3.21 (3 H, s).

(b) 1,4-Diphenyl-1,2-diazabutadiene (**6**) (0.031 g, 0.15 mmol), 120–140 °C, 650 °C,  $1 \times 10^{-3}$  Torr, 30 min; *N*-benzylideneaniline (59%);  $m/z$  181. <sup>1</sup>H n.m.r. spectroscopy and g.c. showed benzylideneaniline to be the only significant product in the pyrolysate;  $\delta_{\text{H}}$  8.44 (1 H, s), 7.9–7.8 (1 H, m), and 7.5–7.1 (8 H, m). The crude, solid pyrolysate was scraped out of the trap and identified by its melting point and mixed melting point (47–50 °C). Unchanged starting material was obtained when the pyrolysis was carried out at 550 °C.

(c) 1-(*o*-Chlorophenyl)-4-phenyl-1,2-diazabutadiene (**7**) (vertical furnace assembly) (0.062 g, 0.26 mmol); 650 °C;  $4.5 \times 10^{-3}$  Torr; *N*-benzylidene-*o*-chloroaniline (14%);  $m/z$  217 ( $M^+$ , 35%), 215 ( $M^+$ , 100), 111 (42), and 77 (52);  $\delta_{\text{H}}$  8.38 (CH=N).

(d) 4-(*p*-Chlorophenyl)-1-phenyl-1,2-diazabutadiene (**8**) (vertical furnace assembly) (0.109 g, 0.45 mmol); 650 °C;  $7 \times 10^{-3}$  Torr; *N*-*p*-chlorobenzylideneaniline (48%);  $m/z$  217 ( $M^+$ , 15%), 215 ( $M^+$ , 44), 104 (14), and 77 (100);  $\delta_{\text{H}}$  8.46 (CH=N).

(e) 1-Phenylazocyclohex-1-ene (**9**) (0.156 g, 0.81 mmol); 45 °C, 600 °C;  $3 \times 10^{-3}$  Torr; 60 min. An i.r. spectrum of the faintly yellow crude pyrolysate indicated the presence of nitrile group(s), but only aniline ( $m/z$  93) could be identified by g.c.-m.s.: the <sup>13</sup>C n.m.r. spectrum showed at least 16 signals in the range  $\delta_{\text{C}}$  16–38. Attempted preparative t.l.c. followed by m.s. of a number of the components showed only oligomeric materials. Starting material was recovered at a furnace temperature of 500 °C.

(f) 1-*p*-Tolylazocyclohexene (**10**) (i) (0.093 g, 0.47 mmol); 80 °C; 600 °C;  $3 \times 10^{-3}$  Torr; 30 min. *p*-Toluidine ( $m/z$ , 107) was the only component identified by g.c.-m.s., and the <sup>13</sup>C n.m.r. spectrum was again very complex in the range  $\delta_{\text{C}}$  16–38. A repeat pyrolysis on a larger scale (0.50 g, 2.5 mmol) gave a quantitative recovery of products which were extracted with hydrochloric acid (1M) to remove basic components. The mass spectrum of the foamy residue showed oligomeric materials ( $m/z$  386, 385) which were not identified.

(ii) (0.049 g, 0.25 mmol); 60–80 °C; 850 °C;  $5 \times 10^{-3}$  Torr; 20 min; *p*-toluidine (28%),  $m/z$  107; 5-methylindole (21%),  $m/z$  131. Yields were somewhat variable, but both products were identical (g.l.c. and <sup>1</sup>H n.m.r.) with authentic samples.

(g) Methyl 3-(phenylazo)but-2-enoate (**11**) (0.163 g, 0.80 mmol); 80–100 °C, 650 °C;  $5 \times 10^{-3}$  Torr; 60 min; the g.c. trace showed two peaks and g.c.-m.s. identified the first peak as aniline  $m/z$  93. The second peak was tentatively identified as methyl glyoxylate anil on the basis of its mass spectrum,  $m/z$  163 ( $M^+$ , 20%), 104 (93), and 77 (100).

(h) Ethyl 3-(phenylazo)but-2-enoate (**12**) (0.130 g, 0.60 mmol), mmol), 100 °C, 650 °C;  $5 \times 10^{-3}$  Torr; 45 min; the g.c. trace showed five peaks and t.l.c. showed six spots, but only aniline could be positively identified by g.c.-m.s.,  $m/z$  93.

(ii) 3-Phenyl-2,3-diazaprop-2-en-1-ones. The orange/red colour of these compounds was a useful indicator for the presence of starting material in the pyrolysate. Thus it was found that 750 °C was the optimum furnace temperature.

(a) 1,3-Diphenyl-2,3-diazaprop-2-en-1-one (**15**) (0.110 g, 0.52 mmol), 130 °C, 750 °C;  $5\text{--}40 \times 10^{-3}$  Torr; 60 min; biphenyl (16%)  $m/z$  154; benzophenone (3%)  $m/z$  182.

This pyrolysis was then repeated on a larger scale and the colourless liquid which had collected in the trap was isolated and shown by g.c.-m.s. to be benzene,  $m/z$  78; owing to its volatility, the yield was not determined.

(b) 3-Phenyl-1-*p*-tolyl-2,3-diazaprop-2-en-1-one (**16**) (0.085 g, 0.38 mmol), 160 °C, 750 °C;  $5\text{--}40 \times 10^{-3}$  Torr; 45 min; biphenyl (4%),  $m/z$  154; 4-methylbiphenyl (4%),  $m/z$  168; 4,4'-dimethylbiphenyl (2%),  $m/z$  182; *p*-toluonitrile (trace)  $m/z$  117.

(c) 1-*o*-Methoxyphenyl-3-phenyl-2,3-diazaprop-2-en-1-one (**17**) (0.023 g, 0.10 mmol); 160 °C, 750 °C;  $5\text{--}30 \times 10^{-3}$  Torr; 45 min; benzaldehyde (28%)  $m/z$  106; biphenyl (2%)  $m/z$  154.

(d) 1-Methyl-3-phenyl-2,3-diazaprop-2-en-1-one (**18**) (0.025 g, 0.17 mmol), 110 °C, 750 °C;  $5\text{--}20 \times 10^{-3}$  Torr; 45 min; it appeared from g.c.-m.s. that biphenyl  $m/z$  154 was present, though this was not quantified.

In the above pyrolysis experiments, benzene (and/or toluene) was almost certainly present, although this was only shown to be the case in example (a). The other pyrolysis experiments were performed on a small scale only, so any benzene (and/or toluene) would have been lost by evaporation during work-up.

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