Thermolysis of Polyazapentadienes. Part 7.[1] An Unambiguous Route to 7-Substituted Quinolines from Cinnamaldehyde Derivatives

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Flash vacuum pyrolysis of the cinnamaldehyde phenylhydrazone derivatives (**4**)—(**6**) or *O*-alkyl oxime derivatives (**7**)—(**12**) at 600—650 °C and 10^{-2}—10^{-3} Torr leads to approximately equal quantities of cinnamonitriles and quinolines. Use of a *p*-substituted cinnamaldehyde derivative gives the appropriate 7-substituted quinoline in high isomeric purity; the reactions take place *via* conjugated iminyl radicals.

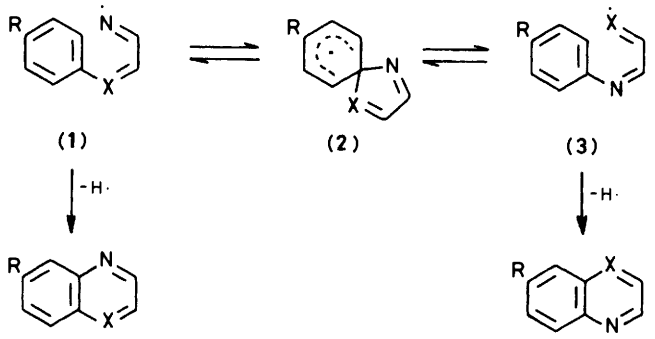
In earlier parts of this series,[2,3] we have reported that the gas-phase cyclisation reactions of aryliminoiminyl radicals (**1**; X = N) can lead to mixtures of products resulting from equilibration *via* the spirodienyl radical (**2**) (Scheme 1; X = N). We now extend this work to arylvinyliminyl radicals (**1**; X = CH), and show that the reduced symmetry of the side-chain causes exclusive formation of just *one* quinoline isomer. Cyclisations of heavily substituted arylvinyliminyl radicals have been observed previously in solution,[4] but these processes are restricted by the requirement for *two* β-aryl groups, to ensure that one aryl group is *cis* to the iminyl function.[5]

Both phenylhydrazones and *O*-alkyl oximes have proved to be satisfactory iminyl precursors in the gas phase:[2] the latter derivatives are particularly attractive from a synthetic point of view, since the products of cyclisation are the only basic materials in the crude pyrolysate, and so can be readily isolated by acid extraction.[6] The range of derivatives (**4**)—(**12**) was therefore chosen to show the effects of free-radical leaving group, substitution in the iminyl side-chain, and substitution in the aromatic ring. All were prepared from the corresponding carbonyl compounds in yields of up to 90%. The liquid *O*-alkyl oximes (**7**)—(**11**) were obtained as mixtures of *syn*- and *anti*-isomers, though the solid *p*-chloro derivative (**12**) was found to be isomerically pure after recrystallisation.

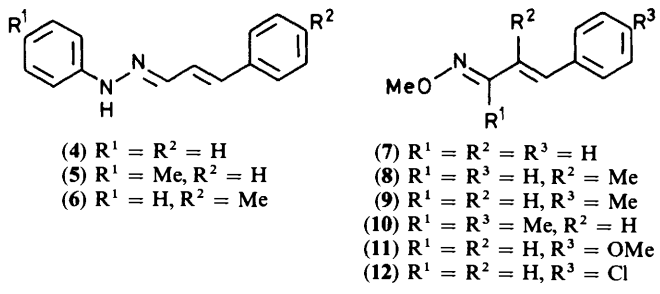
The ^{1}H n.m.r. spectra (100 MHz) of the conjugated segments of the *O*-alkyl oximes (**7**)—(**12**) exhibit a complex two-proton signal centred at δ_H *ca.* 6.7, and an apparent double doublet at *ca.* 7.8 due to the imine proton. The multiplicity of the latter signal is unusual, and was indeed shown to be an artefact due to virtual coupling. Thus the 360 MHz spectrum of the isomerically pure *p*-chloro compound (**12**) had δ_H 7.82 (1 H, d, ^3J 8.78 Hz), 6.77 (1 H, dd, ^3J 16.11 and 8.79 Hz), and 6.70 (1 H, d, ^3J 16.11 Hz), as expected on a first-order basis. The large coupling constant of 16 Hz confirms that the alkene has the *E*-configuration.

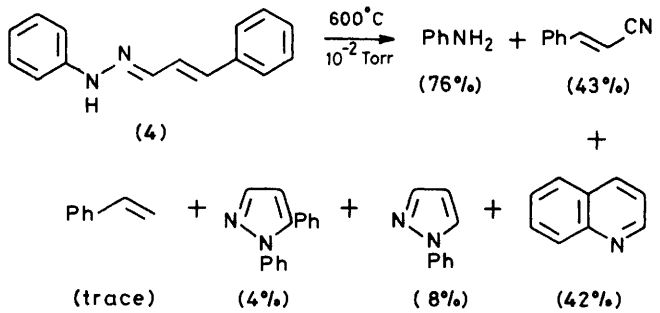
The mass spectra of the hydrazones (**4**)—(**6**) and *O*-alkyl oximes (**7**)—(**12**) show cleavage of the N–N and N–O bonds, respectively, as the major breakdown process, which corresponds to the anticipated thermal fragmentation. In addition, competitive cleavage of the *C*-aryl bond occurs with the hydrazones (**4**)—(**6**): thus the cinnamaldehyde and *p*-methylcinnamaldehyde phenylhydrazones (**4**) and (**6**) both show peaks at *m/z* 145, while the *p*-tolylhydrazone (**5**) has a corresponding fragment at *m/z* 159.

Quinoline (42%), cinnamonitrile (43%), and aniline (76%) are the major products from flash vacuum pyrolysis of the phenylhydrazone (**4**) at 600 °C and 10^{-2} Torr (Scheme 2). Since these are typical conditions for N–N bond cleavage in the gas phase,[7] the mechanism probably involves formation of the iminyl radical (**13**) with subsequent loss of a hydrogen atom. This may either take place directly, to generate the *E*-nitrile, or after isomerisation and cyclisation to generate the quinoline (Scheme 3). Loss of HCN from the iminyl radical (**13**) accounts for the trace of styrene detected in the pyrolysate. It is significant that isomerisation of the *E*-alkene takes place sufficiently readily under these conditions to allow cyclisation (*cf.* references 4 and 5). However, the competitive formation of nitrile is abnormally high in comparison with the pyrolyses of 1,2,5-triazapentadienes, *e.g.* (**14**),[7] and this may reflect the

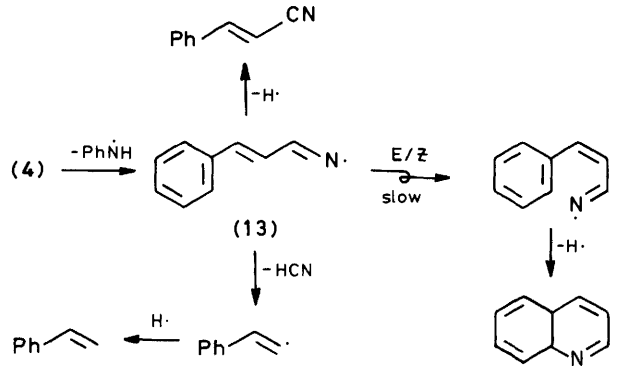


Scheme 1.

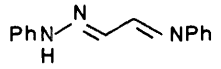




Scheme 2.



Scheme 3.



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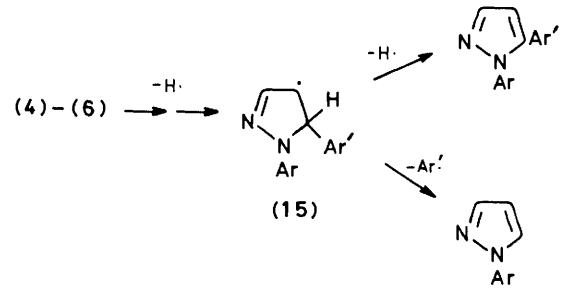
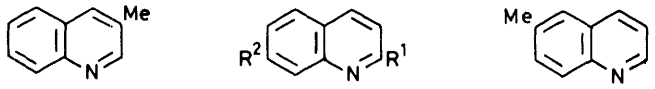


Scheme 4.



(16) (17) R^1 = H, R^2 = Me (18) R^1 = R^2 = Me (19) R^1 = H, R^2 = OMe (20) R^1 = H, R^2 = Cl (21)

higher energy of isomerisation of alkenes relative to imines.* The overall accountance of products is also higher than in the earlier series.[7]

Two minor products, *m/z* 144 and 220, were detected by g.l.c.–mass spectrometry in the pyrolysate of the hydrazone (**4**); these were identified as 1-phenylpyrazole (8%) and 1,5-diphenylpyrazole (4%) by comparison with authentic samples[10-12] (Scheme 2). The absence of the isomeric 3-phenylpyrazole[11] was confirmed similarly. That the *C*-aryl group is lost in the formation of the monoarylpyrazole was confirmed by pyrolysis of the *p*-tolyl derivatives (**5**) and (**6**). Thus the *N*-*p*-tolyl compound (**5**) gave a peak at *m/z* 158 (g.l.c.–mass spectrometry) corresponding to 1-*p*-tolylpyrazole, whereas the *C*-*p*-tolyl derivative (**6**) showed a peak at *m/z* 144 due to 1-phenylpyrazole. The mechanism of formation of these products is not clear at this stage, though the production of two pyrazoles is consistent with an intermediate radical (**15**) which can regenerate conjugation by loss of H˙ or of Ar˙ (Scheme 4).

Pyrolysis of the *O*-alkyl oximes (**7**)—(**12**) followed a similar course to that of the hydrazones, though slightly higher temperatures were needed for complete decomposition (*cf.* reference 2). These precursors had the major advantage that no aniline and no pyrazoles were formed as by-products and so isolation and separation of the quinoline from the styrene and nitriles was readily achieved on a preparative scale. Thus quinoline and 3-methylquinoline (**16**) were obtained in 19 and 27% yields from (**7**) and (**8**), respectively.

Pyrolysis of the *p*-tolyl derivative (**9**) was of particular interest in a mechanistic context, since cyclisation *via* the spirodienyl mechanism (Scheme 1; X = CH) might result in a mixture of 6- and 7-methylquinolines (**21**) and (**17**). In the event, the isolated and redistilled product was pure 7-methylquinoline (**17**) (^{1}H and ^{13}C n.m.r.)[1] and a careful study of the crude basic fraction failed to reveal any trace of the 6-methyl isomer. This suggests either that direct cyclisation occurs, or that *C*–*N* migration from the spirodienyl radical is favoured over *C*–*C* migration. Although conclusive proof in the present series awaits a reliable *gas-phase* method of generating vinyl radicals [*e.g.* (**3**; X = CH)], formation of spirodienyl radicals related to (**2**) *in solution* indeed results in products derived from *C*–*N* migration in most cases.[13,14]

* Isomerisation of imines is notoriously dependent on substituents, but typical activation energies are around 100 kJ mol^{-1}.[8] The corresponding value for alkenes is at least 160 kJ mol^{-1}.[9]

In a similar manner, 2,7-dimethylquinoline (**18**) (21%) was the only basic material obtained from the *O*-alkyl oxime (**10**). This experiment also provides confirmation of the iminyl mechanism, since concerted cyclisation (found for 1,5-diazapentadienes[1]) would result in some side-chain demethylation[1] to give 7-methylquinoline (*m/z* 143). Although two compounds of this molecular weight were detected by g.l.c.–mass spectrometry, both appeared in the neutral fraction and were identified as (*E*)- and (*Z*)-*p*-methylcinnamonitrile by ^{1}H n.m.r. spectroscopy. The unusually high level of *Z*-isomer may be associated with its formation by loss of a methyl group rather than a hydrogen atom, from the iminyl radical.

Despite the considerable efforts which have been devoted to quinoline synthesis,[15] all the practical[16] methods which build a C_3N unit onto a pre-formed benzene ring use substituted anilines as precursors. Indeed, the best available route to 7-substituted quinolines requires cyclisation of a *m*-substituted aniline derivative followed by a tedious separation of the mixture[17] of 5- and 7-substituted quinolines so obtained. The present work offers a direct preparation of 7-substituted quinolines and related fused pyridines[6] from readily available precursors, and with a simple work-up procedure though the overall yields are low. We have applied this approach to the 7-methoxy and 7-chloro derivatives (**19**) and (**20**), both of which were obtained isomerically pure. The rather higher yield obtained in the latter case, has been previously noted with *p*-halogeno substituents in the 1,2,5-triaza series.[18]

Experimental

Unless otherwise stated, ^{1}H and ^{13}C n.m.r. spectra were recorded at 100 and 20 MHz, respectively, for solutions in [^{2}H]chloroform.

Preparation of Substituted Cinnamaldehydes.—These derivatives were made by aldol reaction of the appropriate aromatic aldehyde with acetaldehyde, following literature procedures.[19-21]

Preparation of Hydrazones.—Compounds (**4**)—(**6**), obtained by the action of the hydrazine on the aldehyde in acetic acid solution, were recrystallised from ethanol, and were characterised by m.p.: (**4**), m.p. 165—167 °C (lit.,[22] 168 °C); (**5**), m.p. 152—154 °C (lit.,[23] 155 °C); (**6**), m.p. 141—143 °C (lit.,[19] 145 °C).

Preparation of O-Methyl Oximes.—A suspension of the appropriate aldehyde (50 mmol) and *O*-methylhydroxylamine hydrochloride (4.59 g, 55 mmol) in ethanol (50 ml) containing potassium hydroxide (3.09 g, 55 mmol) was heated under reflux for 15 min. The cooled mixture was poured into water (150 ml) and extracted with methylene chloride (3 × 50 ml). The combined organic extracts were dried (Na_2SO_4), the solvent was removed *in vacuo*, and the residue was distilled (Kugelrohr) to give the *oxime* as a mixture of isomers.

The following 5-aryl-1-methyl-2-aza-1-oxapentadienes were made by this method: 5-*phenyl* (**7**) (90%), b.p. 94—96 °C (0.1 Torr) (Found: C, 74.55; H, 6.95; N, 8.55. $C_{10}H_{11}NO$ requires C, 74.55; H, 6.85; N, 8.7%), δ_H 7.81 (1 H, complex), 7.2—7.5 (5 H, complex), 6.76 (2 H, complex), and 3.92 (minor isomer) and 3.87 (major isomer) (3 H, 2 s), *m/z* 161 (M^+, 53%), 160 (90), 130 (100), 103 (37), 77 (47), and 51 (17); 1,4-*dimethyl*-5-*phenyl* (**8**) (89%), b.p. 94—96 °C (0.1 Torr) (Found: C, 75.65; H, 7.6; N, 7.8. $C_{11}H_{13}NO$ requires C, 75.45; H, 7.45; N, 8.0%), δ_H (200 MHz) 7.85 (1 H, s), 7.2—7.4 (5 H, complex), 6.63 (1 H, s), 3.94 (3 H, s), and 2.13 (3 H, s), *m/z* 175 (M^+, 40%), 174 (88), 144 (100), 115 (64), 91 (28), and 77 (20); 5-p-*tolyl* (**9**) (88%), b.p. 96—99 °C (0.1 Torr) (Found: C, 75.2; H, 7.65; N, 7.9. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.4; N, 8.0%), δ_H 7.79 (1 H, complex), 7.0—7.5 (4 H, complex), 6.74 (2 H, complex), 3.94 (minor isomer) and 3.88 (major isomer) (3 H, 2 s), and 2.30 (3 H, s), *m/z* 175 (M^+, 67%), 174 (100), 144 (72), 143 (56), 115 (39), and 91 (33); 1,3-*dimethyl*-5-p-*tolyl* (**10**) (77%), b.p. 106—110 °C (0.1 Torr) (Found: C, 76.15; H, 8.0; N, 7.6. $C_{12}H_{15}NO$ requires C, 76.2; H, 7.95; N, 7.4%), δ_H (80 MHz) 6.9—7.5 (*ca.* 5 H, complex), 6.80 (>1 H, apparent s), 3.94 (major isomer) and 3.91 (minor isomer) (3 H, 2 s), 2.33 (3 H, s), and 2.09 (minor isomer) and 2.05 (major isomer) (3 H, 2 s), *m/z* 189 (M^+, 50%), 188 (100), 158 (90), 115 (43), 105 (23), 91 (30), and 77 (21); 5-p-*methoxyphenyl* (**11**) (76%), m.p. 79—81 °C (from hexane) (Found: C, 68.9; H, 6.8; N, 7.1. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.8; N, 7.35%), δ_H 7.80 (1 H, complex), 7.32 (2 H, d), 6.82 (2 H, d), 6.68 (2 H, complex), 3.86 (3 H, s), and 3.76 (3 H, s), *m/z* 191 (M^+, 100%), 190 (92), 165 (75), 160 (33), and 159 (58); 5-p-*chlorophenyl* (**12**) [solid isomer, obtained after Kugelrohr distillation at 113—116 °C (0.1 Torr) and trituration with hexane] (56%), m.p. 82—84 °C (from hexane) (Found: C, 61.5; H, 5.4; N, 6.95. $C_{10}H_{10}ClNO$ requires C, 61.4; H, 5.1; N, 7.15%); δ_H 7.82 (1 H, complex), 7.29 (4 H, s), 6.74 (2 H, complex), and 3.90 (3 H, s), *m/z* 197 (M^+, 19%), 196 (38), 195 (62), 194 (100), 166 (27), 164 (73), 102 (27), 101 (35), and 75 (15).

Pyrolysis Experiments.—Small-scale (0.5 mmol) pyrolyses were carried out as previously described,[7] and are reported as follows: compound pyrolysed, quantity, furnace temperature, inlet temperature, pressure range, pyrolysis time, products, and residue. Crude pyrolysates were examined by ^1H n.m.r. spectroscopy, g.l.c. (5% SE30), and g.l.c.–mass spectrometry. All products from the pyrolyses of the 'parent' compounds (**4**) and (**7**) were identical (g.l.c., g.l.c.–mass spectrometry) with authentic samples: products from other experiments were assigned by analogy. Yields are calculated from ^1H n.m.r. spectra, and/or from g.l.c. results after calibration of detector response.

Quinolines were isolated from larger scale (generally 20 mmol) pyrolyses as follows. The total pyrolysate was suspended in ether and filtered through Celite. The filtrate was extracted with dilute hydrochloric acid (1M; 3 × 15 ml). The aqueous extracts were made basic with sodium hydroxide solution (2M) and extracted with methylene chloride (3 × 20 ml). The combined organic extracts were dried (Na_2SO_4), and the solvent was removed *in vacuo* to give the crude quinoline, which was purified by bulb-to-bulb distillation at reduced pressure.

Cinnamaldehyde phenylhydrazone (**4**). 0.098 g (0.44 mmol), 600 °C, 140—160 °C, 3—10 × 10^{-3} Torr, 40 min; styrene (trace), *m/z* 104; aniline (76%), *m/z* 93; quinoline (42%), *m/z* 129; (*E*)-cinnamonitrile (43%), *m/z* 129; 1-phenylpyrazole (8%), *m/z* 144; azobenzene (trace), *m/z* 182; 1,5-diphenylpyrazole (4%), *m/z* 220; residue 0%.

Cinnamaldehyde p-*tolylhydrazone* (**5**). 0.065 g (0.26 mmol), 600 °C, 140—160 °C, 1—5 × 10^{-3} Torr, 40 min; *p*-toluidine (69%), *m/z* 107; quinoline (33%), *m/z* 129; (*E*)-cinnamonitrile (30%), *m/z* 129; 1-*p*-tolylpyrazole (*ca.* 5%), *m/z* 158; 5-phenyl-1-*p*-tolylpyrazole (*ca.* 5%), *m/z* 234; residue 8%.

3-p-*Tolylprop*-2-*enal phenylhydrazone* (**6**). 0.105 g (0.42 mmol), 600 °C, 140—160 °C, 2—5 × 10^{-3} Torr, 25 min; aniline (90%), *m/z* 93; 1-phenylpyrazole (*ca.* 3%), *m/z* 144; 7-methylquinoline (29%), *m/z* 143; (*E*)-*p*-methylcinnamonitrile (34%), *m/z* 143; azobenzene (trace), *m/z* 182; 1-phenyl-5-*p*-tolylpyrazole (*ca.* 4%), *m/z* 234; residue 5%.

1-*Methyl*-5-*phenyl*-2-*aza*-1-*oxapentadiene* (**7**). 0.120 g (0.75 mmol), 650 °C, 40—50 °C, 5 × 10^{-3} Torr, 40 min; styrene (4%), *m/z* 104; quinoline (30%), *m/z* 129; (*E*)-cinnamonitrile (28%), *m/z* 129; residue 6%. Pyrolysis on a preparative scale (20 mmol) with standard work-up, gave quinoline (0.49 g, 19%), b.p. 100—102 °C (16 Torr) (lit.,[15] 238 °C), δ_H (200 MHz) 8.89 (1 H, dd), 8.11 (2 H, complex), 7.79 (1 H, dd), 7.69 (1 H, m), 7.51 (1 H, m), and 7.36 (1 H, dd), δ_C 149.91, 147.86 (q), 135.54, 128.98, 127.84 (q), 127.35, 126.06, and 120.58.

1,4-*Dimethyl*-5-*phenyl*-2-*aza*-1-*oxapentadiene* (**8**). 0.164 g (0.94 mmol), 650 °C, 60—80 °C, 5—30 × 10^{-3} Torr, 25 min; methylstyrene (*ca.* 15%), *m/z* 118; (*E*)- and (*Z*)-2-methyl-3-phenylprop-2-enonitrile (*ca.* 19%), *m/z* 143 and *m/z* 143; 3-methylquinoline (35%), *m/z* 143; residue 0%. Pyrolysis on a larger scale (20 mmol) followed by standard work-up afforded 3-methylquinoline (27%), b.p. 151—153 °C (16 Torr) (lit.,[24] 252—253 °C), δ_H (200 MHz) 8.72 (1 H, d), 8.04 (1 H, d), 7.84 (1 H, br s), 7.68 (1 H, dd), 7.60 (1 H, m), 7.46 (1 H, m), and 2.45 (3 H, s), δ_C 151.99, 146.20 (q), 134.23, 130.04 (q), 128.78, 128.03, 127.74 (q), 126.76, 126.13, and 18.28.

1-*Methyl*-5-p-*tolyl*-2-*aza*-1-*oxapentadiene* (**9**). 0.139 g (0.79 mmol), 650 °C, 60—70 °C, 3—5 × 10^{-3} Torr, 50 min; 7-methylquinoline (20%), *m/z* 143; (*E*)-*p*-methylcinnamonitrile (37%), *m/z* 143; residue 0%. The yield of distilled 7-methylquinoline from a preparative (20 mmol) experiment was 17%, b.p. 141—142 °C (16 Torr) (lit.,[25] 257 °C), δ_H (200 MHz) 8.85 (1 H, dd), 8.07 (1 H, d), 7.87 (1 H, s), 7.68 (1 H, d), 7.35 (1 H, dd), 7.27 (1 H, dd), and 2.55 (3 H, s), δ_C 150.00, 148.23 (q), 139.34 (q), 135.30, 128.43, 128.11, 127.08, 126.02 (q), 119.91, and 21.51. 'Spiking' experiments on the crude basic fraction failed to reveal *any* 6-methylquinoline (^1H n.m.r. at 200 MHz).

1,3-*Dimethyl*-5-p-*tolyl*-2-*aza*-1-*oxapentadiene* (**10**). 0.125 g (0.66 mmol), 650 °C, 80—90 °C, 5 × 10^{-3} Torr, 20 min; *p*-methylstyrene (trace) *m/z* 118; (*Z*)-*p*-methylcinnamonitrile (13%), *m/z* 143; (*E*)-*p*-methylcinnamonitrile (32%), *m/z* 143; 2,7-dimethylquinoline (27%), *m/z* 157; residue 0%. A preparative pyrolysis (20 mmol) with work-up of the basic fraction gave 2,7-dimethylquinoline (21%), b.p. 159—162 °C (16 Torr), m.p. 58—59 °C (from hexane) (lit.,[26] 61 °C), δ_H (80 MHz) 7.96 (1 H, d), 7.80 (1 H, s), 7.64 (1 H, d), 7.29 (1 H, dd), 7.18 (1 H, d), 2.71 (3 H, s), and 2.53 (3 H, s), δ_C 158.66 (q), 147.93 (q), 139.38 (q), 135.58, 127.60, 126.89, 124.29 (q), 120.91, 25.13, and 21.65.

5-p-*Methoxyphenyl*-1-*methyl*-2-*aza*-1-*oxapentadiene* (**11**). 0.090 g (0.47 mmol), 650 °C, 50—70 °C, 3—5 × 10^{-3} Torr, 40 min; *p*-methoxystyrene (trace), *m/z* 134; 7-methoxyquinoline (20%), *m/z* 159; (*E*)-*p*-methoxycinnamonitrile (37%), *m/z* 159; residue 1%. Pyrolysis on a 10 mmol scale gave a 15% yield of distilled 7-methoxyquinoline, b.p. 168—171 °C (16 Torr) [lit.,[17] 153 °C (15 Torr)], δ_H (200 MHz) 8.81 (1 H, dd), 8.04 (1 H, dd), 7.67 (1 H, d), 7.41 (1 H, d), 7.24 (1 H, dd), 7.18 (1 H, dd), and 3.94

(3 H, s), δ_C 160.41 (q), 150.27, 149.76 (q), 135.35, 128.51, 123.26 (q), 119.50, 118.70, 107.13, and 55.19.

5-p-*Chlorophenyl*-1-*methyl*-2-*aza*-1-*oxapentadiene* (**12**). 0.089 g (0.45 mmol), 650 °C, 70 °C, 5×10^{-3} Torr, 30 min; *p*-chlorostyrene (2%), *m*/*z* 138 and 140; 7-chloroquinoline (36%), *m*/*z* 163 and 165; (*E*)-*p*-chlorocinnamonitrile (31%), *m*/*z* 163 and 165; residue 4%. Pyrolysis on a 5 mmol scale, with standard work-up, gave 7-chloroquinoline (34%), b.p. 159—162 °C (16 Torr) (lit.,[25] 267—268 °C), δ_H (200 MHz), 8.91 (1 H, dd), 8.10 (2 H, complex), 7.74 (1 H, d), 7.49 (1 H, dd), and 7.13 (1 H, dd), δ_C 151.04, 148.29 (q), 135.51, 134.96 (q), 128.73, 128.18, 127.29, 126.32 (q), and 120.95.

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