Factors Affecting Rates of Thermal Decomposition of 5-Azidopyrazoles: A Comparison with other Aromatic Azides

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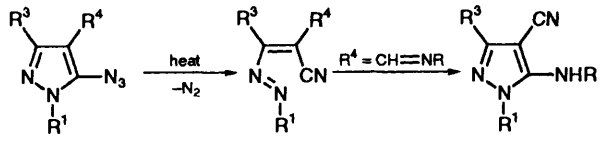
2-Methoxyazidobenzene has been used as a model compound for α-azido five-membered heterocycles, and undergoes thermal loss of nitrogen 16 times as fast as azidobenzene and 3.6 times as fast as its *para* isomer. These rates identify an important electrostatic stabilization within a charge-separated transition state. It is argued that this stabilization would be very much larger in thermolyses of α-azido five-membered heterocycles and removes the need to postulate that their high rates are due to appreciable ring-opening at the transition state. Electronic effects of ring substituents in 5-azidopyrazoles are consistent with this electrostatic model. The electron distribution required is not compatible with the operation of a neighbouring group effect, and none is found for 5-azido-4-nitro-pyrazole.

The high rates of thermal decomposition of α-azido five-membered heterocycles are well known phenomena. Whereas simple azidobenzenes require temperatures of about 160 °C to achieve a half-life of 1 h,[1,2] many α-azidoheterocycles can decompose to this extent at 60 °C, and some even at ambient temperatures. Qualitative reports of these facile decompositions abound in the literature for the α-azides of furans, thiophenes, oxazoles, pyrazoles, triazoles, benzofurans, benzothiophenes and benzopyrroles; recent reviews have summarized these data.[3,4] A limited number of rate constants have been reported for 2-azidofurans,[5] 2-azidothiophenes,[6,7] 5-azido-1,2,3-triazoles,[8] 2-azidobenzothiophene,[9a] 2-azidobenzofuran[9b] and 2-azido-1-methylindole.[9b] β-Azidothiophenes also lose nitrogen more rapidly than the azidobenzenes though the relative rate factors are much smaller than for α-azidothiophenes.[6,7,10]

In addition to the remarkably high rates of thermal decomposition, the thermolysis products of the α-azido five-membered heterocycles are unusual. Most of them are the result of ring-opening to form nitrilic heterodienes which in some cases reclose to yield new heterocycles. A published reaction is shown in Scheme 1.[11]



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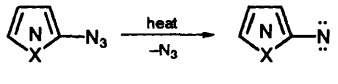
Scheme 1

In view of the very high rates of nitrogen loss from the α-azidoheterocycles, recent reviewers[3,4] of the field have suggested that the ring-opening and nitrogen loss may be a concerted process in which the high-energy nitrene species **2** (Scheme 2) is never formed. In particular, Spinelli and Zanirato[7] have reported that 3-azidothiophene undergoes



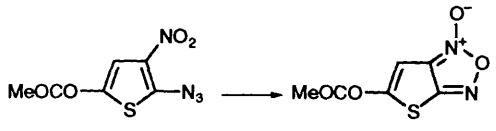
(X = O, S, Se, NR) **2**

Scheme 2

† On sabbatical leave from the University of Newcastle, Australia.

thermolysis with a moderately high activation energy (128 kJ mol^{-1}) and yields nitrene-derived products, while 2-azidothiophene has a much lower activation energy (94 kJ mol^{-1}) and yields products *via* ring-opening. On these grounds, the authors have supported a concerted ring-opening with nitrogen loss for the 2-azidothiophene.

There are however, also reports of products derived from α-azides which are clearly derived from formal nitrenes which ring-close onto an adjacent substituent with retention of the original ring.[6,12,13] For instance, in the case of methyl 2-azido-3-nitrothiophene-5-carboxylate, there is no evidence of ring-opening at all, the only product being the corresponding furazan oxide (Scheme 3),[6] and a high level of neighbouring



Scheme 3

group participation of the nitro group was claimed. Hence, the situation concerning the concertedness of ring-opening and nitrogen loss is not at all clear.

We have now studied a large number of 5-azidopyrazoles in an attempt to resolve three important issues. Firstly, we will address the question of whether ring-opening is concerted with, or subsequent to, the thermal loss of nitrogen. Secondly, we will examine the role which electronic factors may play in these very high rates of nitrogen loss from α-azidopyrazoles. Thirdly, there is the question of whether neighbouring group participation can take place in these inherently fast azide thermolyses.

Discussion

The substantial body of rate and product data assembled here go a considerable distance towards answering the questions we have formulated, and identify a new factor which can stabilize the transition state in the step of nitrogen loss. We will present the results in terms of the original questions and explore the extent to which we can answer them.

Why do α-Azido Five-membered Heterocycles Thermolyse so Fast?—In Table 1 we compare the rate constant of thermal decomposition of 5-azido-3-methyl-1-phenylpyrazole with published data for azidobenzene[14] and the azidothiophenes.[7]

Table 1 Rate constants (calculated at 80 °C) for thermal decomposition

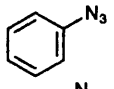
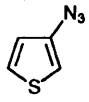
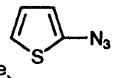
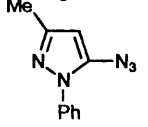
Azido compound	k_1/s^{-1}	k_{rel}	Solvent	Ref.
	4.57×10^{-8}	1	Decalin	14
	1.35×10^{-6}	30	*p*-Chlorotoluene	7
	3.08×10^{-3}	67 400	*p*-Chlorotoluene	7
	1.67×10^{-4}	3655	*p*-Xylene	This work

Table 2 Solvent effect on the rate of thermolysis of 5-azido-3-methyl-1-phenylpyrazole at 80 °C (rates measured by the ^1H NMR method)

Solvent	$k_1/10^{-5}\ s^{-1}$
$C_6D_5CD_3$	11.5
$CDCl_2$–$CDCl_2$	10.6
[$^2H_8$]Dioxane	9.8
$(CD_3)_2SO$	10.4

Table 3 Rates and Arrhenius parameters for the thermal decomposition of 2-methoxy- and 2-(methylthio)-azidobenzene in decalin

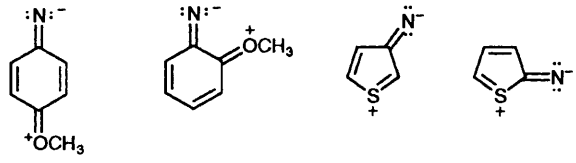
T/°C	$k_1/10^{-5}\ s^{-1}$ [a]	Parameter[b]
2-Methoxyazidobenzene		
120.0	5.97, 6.16	$E_{act} = 138.9 \pm 0.6$ kJ mol^{-1}
130.0	18.0, 18.1	$S_{act} = 16.9 \pm 1.5$ J mol^{-1} K^{-1}
140.0	48.3, 48.3	$\ln A = 32.8 \pm 2.0$
150.0	125, 123	$k_{rel} = 16.0$[c]
2-(Methylthio)azidobenzene		
123.0	6.26	$E_{act} = 133.0 \pm 1.5$ kJ mol^{-1}
124.3	7.44	$S_{act} = -0.3 \pm 3.8$ J mol^{-1} K^{-1}
130.4	13.0	$\ln A = 30.7 \pm 5.1$
130.5	12.7	$k_{rel} = 12.2$[c]
137.7	26.3, 28.3	
145.1	53.6, 52.3	

[a] A free radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, was added to all runs. Varying the ratios from 1.2 to 2.7 mol/mol azide did not affect the values of the rate constants. [b] Errors are expressed as 90% confidence limits. [c] k_{rel} is with respect to the value $k_1 = 3.78 \times 10^{-6}\ s^{-1}$ for azidobenzene at 120 °C (see ref. 14).

Unfortunately, there is no common solvent but the solvent effects on reaction rates have been shown to be small[6] (see also Table 2).

A common feature of the thermolyses of azidoheterocycles is their very high rates compared with that of azidobenzene. In view of the formation of ring-opened products from 2-azidothiophene, it is not surprising that Spinelli and Zanirato[7] suggested that the transition state resembles ring-opened products rather than α-nitrenothiophene. However, our data for 2-methoxy- and 2-(methylthio)-azidobenzene (see Table 3) suggest an alternative explanation.

Whereas the methoxy group in the 4-position of azidobenzene is known to increase the thermolysis rate by a factor of 4.5, in the *ortho* position it has a much larger effect (a factor of 16). In the *para* substituted compound the rate increase has been attributed to stabilization of the transition state on account of the conjugated nitrene **3**. We now propose that the *ortho* methoxy group exerts its still larger stabilizing effect because of the electrostatic attraction between the adjacent charges (see structure **4**). The *ortho* methylthio group exerts a similar effect, the rate enhancement being slightly smaller (a factor of 12.2). One can extend this proposal to the two azidothiophenes (Table 1). The stabilization represented by structure **5** is similar to that in 4-methoxyphenylnitrene, though it is expected to be larger because endocyclic sulfur exerts larger conjugative effects.[15] In turn, this larger conjugative effect must produce a larger electrostatic attraction in the isomeric nitrene **6**. We suggest that this electrostatic stabilization of the nitrene-like transition state is a significant factor in determining rates of thermolysis of all α-azido five-membered heterocycles.



3 **4** **5** **6**

A better perspective is obtained by converting the rate enhancements into energy terms. Using the Arrhenius equation, and assuming approximately equal values of the *A*-term, we have calculated the extents to which various transition states are more stable than the one for thermolysis of azidobenzene. The values for 2-methoxyazidobenzene, 2-azidothiophene and 5-azido-3-methyl-1-phenylpyrazole are 8, 33 and 26 kJ mol^{-1}, respectively. The largest stabilization is only four times as large as that found in 2-methoxyazidobenzene and, in view of the greater contribution from structures such as **6** for these heterocyclic nitrenes, and the dependence of the electrostatic attraction on the square of the magnitude of the charge, it is not impossible that our simple electrostatic model can explain the very high reactivities of the α-azido five-membered heterocycles.

The above argument does not prove that there is no component of ring-opening at the transition state in certain cases, but it does reduce the compulsion to argue that only ring-opening can explain such high rates of thermolysis. For the purposes of the following discussion, we shall assume that all our azides have formed an electrostatically stabilized nitrene in the rate-determining step, and that any ring-opening has occurred subsequently.

Effects of Ring Substituents on Reaction Rates for 5-Azidopyrazoles.—It would be expected that, if azidopyrazoles **1** undergo pyrolysis *via* a stabilized nitrene **7**, there would be significant effects of changing the substituents at the 1-position.

Table 4 Effect of 1-substituents on rates of thermolysis of 5-azidopyrazoles **1**; solvent: *p*-xylene (rates measured by the IR method)

	R^1	R^3	R^4	T/°C	Mean $k_1/10^{-5}$ s^{-1} [a]
1a	Ph	Me	CHO	80	8.78 (8.28)
1b	*p*-$NO_2C_6H_4$	Me	CHO	80	4.21 (4.08)
1c	Ph	Ph	CHO	80	3.82 (3.96)
1d	Me	Ph	CHO	80	3.22
1e	Ph	Me	CH=NPh	80	64.8
				60	5.27
1f	*p*-$MeOC_6H_4$	Me	CH=NPh	80	91.5
				60	8.04
1g	*p*-$NO_2C_6H_4$	Me	CH=NPh	80	34.4

[a] Measured on the azido band in the IR spectrum; the values in parentheses were measured on the aldehyde carbonyl band; the figures quoted are the average from duplicate runs.

Table 5 Effects of 3-substituents on rates of thermolysis of 5-azido-1-phenyl-4-(phenyliminomethyl)pyrazoles **1** (R^1 = Ph, R^4 = CH=NPh) at 80 °C; solvent: *p*-xylene (rates measured by the IR method)

	R^3	Mean $k_1/10^{-5}$ s^{-1} [a]
1h	H	42.1
1e	Me	64.8
1i	Bu^t	41.9
1j	Ph	16.8
1k	CF_3	5.57
1l	COOMe	4.55

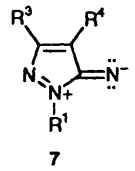
[a] Duplicate runs were performed, the mean deviation from the quoted values being 2.1%.

Table 6 Effect of 4-substituents on the rates of thermolysis of 5-azido-3-methyl-1-phenylpyrazoles **1** (R^1 = Ph, R^3 = Me)

	R^4	T/°C	$k_1/10^{-5}$ s^{-1} [a]
1m	H	80	16.7
1n	Ph	60	25.9
1o	CN	80	8.69
1a	CHO	80	8.78
1e	CH=NPh	80	64.8
		60	5.27
1p	CH=N–NHCOOEt	60	32.8
1q	CH=CHCOOEt(*E*)	60	30.2
1r	NO_2	80	2.01

[a] Rates were measured in *p*-xylene by the IR method, except for **1n** and **1q** which were measured in deuteriated toluene by the ^{1}H NMR method.

In particular, one would predict that electron-releasing substituents R^1 would increase the rate. The results of changing R^1, for a range of R^3 and R^4 groups, are collected in Table 4. The expected rate order of *p*-methoxyphenyl > phenyl > *p*-nitrophenyl and phenyl > methyl is found, but the effects are very small. Smith and coworkers[8] have reported a similar small effect for changing the 1-aryl group in 5-azido-1,2,3-triazoles. Both these results are actually consistent with our postulate of electrostatic stabilization in **7**: whereas conjugating groups R^1



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increase the extent of charge separation, the positive charge density will be dispersed by groups like *p*-methoxyphenyl so that the electrostatic attraction between the opposite charges is not much affected.

The 3-substituents are not expected to exert large direct effects on the rate, but their influence on the electron density in the heteroaromatic ring must affect the extent to which this ring can act as an electron donor to the nitrene centre. Thus, electron-attracters should decrease the rate, and the observed rate order Me > H, Bu^t > Ph > CF_3 > COOMe is the expected one (see Table 5).

A wide range of 4-substituents has been studied (Table 6), but many of these are potential neighbouring groups and are best examined under that heading.

Do Neighbouring Group Effects Operate in α-Azidopyrazoles?—The observed order of rate for these 4-substituents (with due allowance for different temperatures of measurement) is as follows: CH=N–NHCOOEt, CH=CHCOOEt > Ph > CH=NPh > H > CN, CHO > NO_2. Of these groups, only four have had their neighbouring group effects assessed for azidobenzenes, where the order of effectiveness is NO_2 > CH=NPh > CHO > CH=NNHPh, and cyano is not effective at all.[14] From Table 6 it is clear that formyl is no more effective than cyano, and nitro is less effective than either of them. The failure of nitro in particular to accelerate the rate is a clear indication that neighbouring group effects are absent in these systems. In the case of the 4-phenyliminomethyl group, we have found a positive entropy of activation (see Table 7), which is at variance with the negative values found for all known neighbouring group effects in azidobenzene thermolysis.[1] In a broad sense the deactivating effect of the strong electron-attracting groups (nitro, formyl, cyano) is consistent with a nitrene **7** as intermediate, which is destabilized when the electron-density of the ring is decreased. Further work will be required to determine the relative importance of resonance, inductive, and steric effects operating from the 4-position.

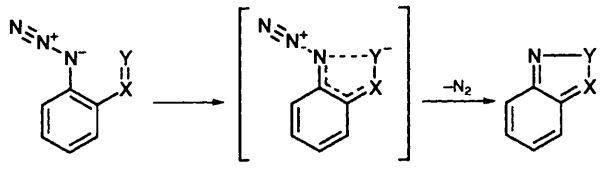
The absence of neighbouring group effects in the pyrolysis of 5-azidopyrazoles deserves special comment, especially in view of the published claim[6] that the nitro group in methyl 2-azido-3-nitrothiophene-5-carboxylate exerts a very large effect of this type (see Scheme 3). However, the rate constant for this compound in methanol solution at 45 °C (k_1 = 3.97 × 10^{-5} s^{-1}) is actually not high when compared with the value of k_1 = 9.08 × 10^{-5} s^{-1} (*p*-chlorotoluene solution, same temperature) which has since been published for 2-azidothiophene.[7] Even if a degree of uncertainty for the different solvent and the influence of the methoxycarbonyl group are allowed for, there cannot be significant assistance from the nitro group here, whereas this group is reported to enhance the rate for azidobenzene by a factor of 1060.

The lack of a neighbouring group effect in 4-substituted-5-azidopyrazoles (and 2-azidothiophenes) can be understood in terms of the transition state **8** which one of us has postulated for neighbouring group participation in azidobenzene thermolysis.[16] The preferred transition state requires considerable conjugation between the azido group and the neighbouring group, so that the latter has negative charge on its terminal atom with which it can initiate a bond to the essentially neutral

Table 7 Arrhenius parameters for thermal decomposition of 5-azido-3-methyl-1-phenyl-4-(phenyliminomethyl)pyrazole **1e**; solvent: *p*-xylene

T/°C	$k_1/10^{-5}$ s^{-1}	Parameter[a]
60.0	5.29, 5.25	E_{act} 121.6 ± 0.8 kJ mol^{-1}
70.0	20.5, 19.5	S_{act} = 28.9 ± 2.4 J mol^{-1} K^{-1}
80.0	63.3, 66.2	ln A = 34.1 ± 2.3
90.0	200, 200	

[a] Errors are expressed as 90% confidence limits.



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Transition state

Scheme 4

inner nitrogen of the azido group. This charge distribution, and the conjugation implied by it, are incompatible with the charge distribution (as in **7**) which we propose is the explanation for the very high rates of nitrogen loss from all α-azido five-membered heterocycles. We have recently advanced the same explanation for the lack of appreciable neighbouring group effects in the thermolysis of β-azidothiophenes.[10]

In the case of an α-azidothiophene with an adjacent nitro group, it is reported that a furazan oxide was obtained (Scheme 3).[6] As explained above, we do not believe that this product is the result of a neighbouring group effect, in which case it must arise by internal capture of the nitrene by the nitro group. In principle, the 5-azidopyrazoles with suitable 4-substituents (nitro, formyl, phenylimino) could yield bicyclic products by the same route, but in practice all of the intermediate nitrenes have undergone opening of the pyrazole ring (see the Experimental section). The factors determining this preference are not yet understood.

Conclusions

Our postulate of electrostatic stabilization of the transition state for nitrogen loss from α-azido five-membered heterocycles is compatible with the wide range of kinetic data assembled here. In our view, this transition state resembles a nitrene and there is no compelling reason to postulate that significant ring-opening has occurred by that stage. On this model of the reaction pathway, the ultimate products (whether ring-opened, or produced by reactions of the nitrene with an adjacent substituent or with solvent) are formed in subsequent steps from this electrostatically stabilized nitrene. The factors which determine why this nitrene often ring-opens are currently being explored.

Experimental

M.p.s were determined using a Reichert Thermovar apparatus. IR spectra of the products were recorded on a Perkin-Elmer 1720 FT spectrometer, NMR spectra on a Bruker WM-250 or AMX-400 spectrometer, and mass spectra (EI) on a Hewlett Packard 5989 A or Kratos MS50 TC (for high resolution) instrument, operating at 70 eV. *J* values are recorded in Hz.

The azides **1a**, **1c**, **1d**, **1m**, **1n** and **1p**, and their decomposition products have been reported.[11,13,17] The other azides were prepared from the corresponding 5-chloropyrazoles (5-aminopyrazole for **1q**) by analogous procedures and gave single products on thermolysis (except **1b** and **1r**) consistent with the reported pathways. The products are azoacrylonitriles when $R^4 \neq$ CHO or CH=NR, 4-cyano-5-hydroxypyrazoles when R^4 = CHO and 4-cyano-5-aminopyrazoles when R^4 = CH=NR according to Scheme 1. For preparative purposes the thermolysis reactions were carried out in refluxing carbon tetrachloride, and the reported yields are those obtained after chromatographic purification and recrystallization.

5-Azido-3-methyl-1-(p-nitrophenyl)pyrazole-4-carbaldehyde **1b**.—Prepared by nitration of pyrazole **1a** in 54% yield, m.p. 130.5–132 °C (from $CHCl_3$–Et_2O) (Found: C, 48.5; H, 3.0. $C_{11}H_8N_6O_3$ requires C, 48.53; H, 2.96%); ν_{max}(KBr)/cm^{-1} 2155s (N_3), 1675s (CHO), 1523s and 1339s (NO_2); δ_H($CDCl_3$) 2.55 (3 H, s, Me), 7.95 and 8.35 (4 H, 2 d, *p*-$NO_2C_6H_4$) and 9.95 (1 H, s, CHO); δ_C($CDCl_3$) 12.8 (Me), 113.0 (C-4), 123.8, 124.6, 142.1 and 146.5 (*p*-$NO_2C_6H_4$), 141.3 (C-5), 153.1 (C-3) and 183.7 (CO); *m*/*z* 272 ($M^{\bullet+}$, 2%), 244 ($M^{\bullet+}$ − N_2, 12) and 50 (100).

This compound thermolysed to an intractable black tar having an IR absorption at 2235 cm^{-1} (CN) and no aldehyde function.

5-Azido-3-methyl-1-phenyl-4-(N-phenyliminomethyl)pyrazole **1e**.—Prepared from pyrazole **1a** and aniline in 61% yield, m.p. 68 °C (lit.,[18] 68 °C); ν_{max}(KBr)/cm^{-1} 2146s (N_3) and 1625s (C=N); δ_H($CDCl_3$) 2.48 (3 H, s, Me), 7.19–7.65 (10 H, m, 2 Ph) and 8.44 (1 H, s, CH=N); δ_C($CDCl_3$) 13.0 (Me), 110.9 (C-4), 120.8, 124.1, 125.7, 127.9, 129.0, 129.2, 137.8 and 152.1 (2 Ph), 150.4 (C-3), 137.0 (C-5) and 150.8 (CH=N, $^1J_{CH}$ 157.6); *m*/*z* 302 ($M^{\bullet+}$, 1.5%), 274 ($M^{\bullet+}$ − N_2, 30) and 77 (Ph^+, 100).

This compound thermolysed to 5-anilino-4-cyano-3-methyl-1-phenylpyrazole; yield 50%, m.p. 146 °C (from *c*-C_6H_{12}) (Found: C, 74.3; H, 5.3. $C_{17}H_{14}N_6$ requires C, 74.43; H, 5.14%); ν_{max}(KBr)/cm^{-1} 3300s (NH) and 2210s (CN); δ_H($CDCl_3$) 2.40 (3 H, s, Me), 6.05 (1 H, br s, NH) and 6.95–7.50 (10 H, d + 2 t + 2 m, 2 Ph); δ_C($CDCl_3$) 13.1 (Me), 82.1 (C-4), 113.5 (CN), 119.0, 123.7, 124.3, 128.7, 129.4, 129.7, 137.2 and 139.5 (2 Ph), 145.9 (C-5) and 152.1 (C-3); *m*/*z* 274 ($M^{\bullet+}$, 100%).

5-Azido-1-(p-methoxyphenyl)-3-methyl-4-(N-phenyliminomethyl)pyrazole **1f**.—Prepared from the corresponding azido aldehyde and aniline in 75% yield, m.p. 92–93 °C (from CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 2140s (N_3) and 1650s (C=N); δ_H($CDCl_3$) 2.52 (3 H, s, Me), 3.90 (3 H, s, MeO), 7.03 and 7.55 (4 H, 2 d, *p*-$MeOC_6H_4$), 7.2–7.3 and 7.45 (5 H, m + t, Ph) and 8.48 (1 H, s, CH=N); δ_C($CDCl_3$) 13.0 (Me), 55.5 (MeO), 110.6 (C-4), 114.2, 125.8, 130.8 and 159.3 (*p*-$MeOC_6H_4$), 120.8, 125.7, 129.2 and 152.2 (Ph), 137.0 (C-5), 150.1 (C-4) and 150.9 (CH=N, $^1J_{CH}$ 158); *m*/*z* 332 ($M^{\bullet+}$, 3%), 304 ($M^{\bullet+}$ − N_2, 44) and 77 (Ph^+, 100) (Found: $M^{\bullet+}$, 332.1376. $C_{18}H_{16}N_6O$ requires *M*, 332.1386).

This compound thermolysed to 5-anilino-4-cyano-1-(*p*-methoxyphenyl)-3-methylpyrazole; yield 89%, m.p. 121–122 °C; ν_{max}(KBr)/cm^{-1} 3240m (NH) and 2224s (CN); δ_H($CDCl_3$) 2.36 (3 H, s, Me), 3.81 (3 H, s, MeO), 6.00 (1 H, br s, NH), 6.93 and 7.36 (4 H, 2 d, *p*-$MeOC_6H_4$), 6.97, 7.05 and 7.28 (5 H, d + 2 t, Ph); δ_C($CDCl_3$) 13.0 (Me), 55.5 (MeO), 81.4 (C-4), 113.6 (CN), 114.8, 126.1, 129.8 and 159.7 (*p*-$MeOC_6H_4$), 118.9, 123.6, 129.4 and 139.5 (Ph), 145.9 (C-5) and 151.7 (C-3); *m*/*z* 304 ($M^{\bullet+}$, 77%) and 77 (Ph^+, 100) (Found: $M^{\bullet+}$, 304.1323. $C_{18}H_{16}N_4O$ requires *M*, 304.1324).

5-Azido-3-methyl-1-(p-nitrophenyl)-4-(N-phenyliminomethyl)pyrazole **1g**.—Prepared from **1b** in 91% yield, m.p. 121 °C (from EtOH); ν_{max}(KBr)/cm^{-1} 2149s (N_3); δ_H($CDCl_3$) 2.5 (3 H, s, Me), 7.2–7.45 (5 H, 2 m, Ph), 7.95 and 8.30 (4 H, 2 d, *p*-$NO_2C_6H_4$) and 8.45 (1 H, s, CH=N); δ_C($CDCl_3$) 13.1 (Me),

112.1 (C-4, $^2J_{CH}$ 12, $^3J_{CH}$ 2.5), 120.9, 126.2, 129.4 and 151.8 (Ph), 123.4, 124.8, 142.9 and 146.1 (*p*-$NO_2C_6H_4$), 137.7 (C-5, $^3J_{CH}$ 7), 150.3 (CH=N, $^1J_{CH}$ 158.6) and 151.8 (C-3); *m/z* (no $M^{\bullet+}$), 319 ($M^{\bullet+} - N_2$, 16%) and 77 (Ph^+, 100).

This compound thermolysed to 5-anilino-4-cyano-3-methyl-1-(*p*-nitrophenyl)pyrazole; yield 77%, m.p. 171 °C; ν_{max}(KBr)/cm^{-1} 3241s (NH) and 2218s (CN); δ_H($CDCl_3$) 2.40 (3 H, s, Me), 6.40 (1 H, br s, NH), 6.87, 7.02 and 7.24 (5 H, d + 2 t, Ph), 7.77 and 8.20 (4 H, 2 d, *p*-$NO_2C_6H_4$); δ_C($CDCl_3$) 13.1 (Me), 84.9 (C-4), 112.8 (CN), 118.4, 123.9, 129.6 and 139.5 (Ph), 123.4, 124.8, 142.6 and 146.2 (*p*-$NO_2C_6H_4$), 146.7 (C-5) and 153.2 (C-3); *m/z* 319 ($M^{\bullet+}$, 100%).

5-Azido-1-phenyl-4-(N-phenyliminomethyl)pyrazole **1h**.—Prepared from the corresponding azido aldehyde and aniline in 71% yield, m.p. 87 °C (from EtOH) (Found: C, 66.65; H, 4.3. $C_{16}H_{12}N_6$ requires C, 66.66; H, 4.20%); ν_{max}(KBr)/cm^{-1} 2148s, (N_3) and 1625s (C=N); δ_H($CDCl_3$) 7.15–7.7 (10 H, 2 t + d + m, 2 Ph), 7.95 (1 H, s, 3-H) and 8.45 (1 H, s, CH=N); δ_C($CDCl_3$) 113.4 (C-4), 120.8, 124.2, 125.9, 128.2, 129.0, 129.2, 137.8 and 151.8 (2 Ph), 136.7 (C-5), 141.8 (C-3) and 150.5 (CH=N); *m/z* 288 ($M^{\bullet+}$, 1%), 260 ($M^{\bullet+} - N_2$, 30) and 77 (Ph^+, 100).

This compound thermolysed to 5-anilino-4-cyano-1-phenylpyrazole; yield 65%, m.p. 159 °C (Found: C, 73.7; H, 4.6. $C_{16}H_{12}N_4$ requires C, 73.81; H, 4.65%); ν_{max}(KBr)/cm^{-1} 3199m (NH) and 2219s (CN); δ_H($CDCl_3$) 6.95–7.6 (10 H, d + 2 t + m, 2 Ph) and 7.86 (1 H, s, 3-H); δ_C($CDCl_3$) 82.2 (C-4), 113.0 (CN), 119.2, 124.0, 124.5, 129.0, 129.5, 129.6, 137.2 and 139.5 (2 Ph), 142.5 (C-3, $^1J_{CH}$ 194) and 145.9 (C-5); *m/z* 260 ($M^{\bullet+}$, 100%).

5-Azido-3-tert-butyl-1-phenyl-4-(N-phenyliminomethyl)pyrazole **1i**.—Prepared from the corresponding azido aldehyde in 87% yield, m.p. 87 °C (Found: C, 69.7; H, 5.9. $C_{20}H_{20}N_6$ requires C, 69.74; H, 5.85%); ν_{max}(KBr)/cm^{-1} 2140s (N_3) and 1620m (C=N); δ_H($CDCl_3$) 1.5 (9 H, s, Bu^t), 7.2–7.65 (10 H, 2 d + t + m, 2 Ph) and 8.8 (1 H, s, CH=N); δ_C($CDCl_3$) 30.4 and 34.0 (Bu^t), 109.9 (C-4), 120.9, 124.2, 125.7, 127.7, 128.9, 129.2, 138.0 and 152.2 (2 Ph), 137.5 (C-5), 152.5 (CH=N, $^1J_{CH}$ 159) and 160.7 (C-3); *m/z* 344 ($M^{\bullet+}$, 2.6%), 316 ($M^{\bullet+} - N_2$, 88) and 301 ($M^{\bullet+} - N_2$ – Me, 100).

This compound thermolysed to 5-anilino-3-*tert*-butyl-4-cyano-1-phenylpyrazole; yield 97%, m.p. 151 °C (from *n*-C_6H_{14}–Et_2O) (Found: C, 75.9; H, 6.35. $C_{20}H_{20}N_4$ requires C, 75.92; H, 6.37%); ν_{max}(KBr)/cm^{-1} 3300s (NH) and 2220s (CN); δ_H($CDCl_3$) 1.5 (9 H, s, Bu^t), 5.9 (1 H, br s, NH) and 6.9–7.6 (10 H, 2 d + 3 t, 2 Ph); δ_C($CDCl_3$) 29.1 and 33.8 (Bu^t), 81.0 (C-4), 114.5 (CN), 118.1, 123.1, 124.1, 128.4, 129.4, 129.6, 137.5 and 140.2 (2 Ph), 146.8 (C-5) and 162.9 (C-3); *m/z* 316 ($M^{\bullet+}$, 100%).

5-Azido-1,3-diphenyl-4-(N-phenyliminomethyl)pyrazole **1j**.—Prepared from **1c** and aniline in 50% yield, m.p. 133 °C (from EtOH) (Found: C, 72.7; H, 4.5. $C_{22}H_{16}N_6$ requires C, 72.50; H, 4.43%); ν_{max}(KBr)/cm^{-1} 2140s (N_3) and 1630s (C=N); δ_H($CDCl_3$) 7.15–7.55, 7.67 and 7.71 (15 H, m + 2 d, 3 Ph) and 8.55 (1 H, s, CH=N); δ_C($CDCl_3$) 110.5 (C-4), 120.9, 124.5, 125.9, 128.2–129.2, 132.0, 137.8 and 151.8 (3 Ph), 137.5 (C-5), 152.1 (CH=N) and 153.5 (C-3); *m/z* (no $M^{\bullet+}$), 336 ($M^{\bullet+} - N_2$, 100%).

This compound thermolysed to 5-anilino-4-cyano-1,3-diphenylpyrazole; yield 65%, m.p. 129 °C (from toluene) (Found: C, 78.7; H, 4.9. $C_{22}H_{16}N_4$ requires C, 78.54; H, 4.80%); ν_{max}(KBr)/cm^{-1} 3304s (NH) and 2233s (CN); δ_H($CDCl_3$) 6.35 (1 H, s, NH), 6.95, 7.56, 8.05, 7.05, 7.27 and 7.32–7.50 (15 H, 3 d + 2 t + m, 3 Ph); δ_C($CDCl_3$) 81.2 (C-4), 114.2 (CN), 118.4, 123.3, 124.3, 126.7, 128.8–130.8, 137.3 and 140.0 (3 Ph), 147.3 (C-5) and 152.5 (C-3); *m/z* 336 ($M^{\bullet+}$, 100%).

5-Azido-1-phenyl-4-(N-phenyliminomethyl)-3-trifluoromethylpyrazole **1k**.—Prepared from the corresponding azido aldehyde in 49% yield, m.p. 76 °C (from EtOH) (Found: C, 57.2; H, 3.2. $C_{17}H_{11}F_3N_6$ requires C, 57.31; H, 3.11%); ν_{max}(KBr)/cm^{-1} 2150s (N_3) and 1630s (C=N); δ_H($CDCl_3$) 7.24–7.28, 7.41, 7.46, 7.52 and 7.63 (10 H, m + 3 t + d, 2 Ph) and 8.56 (1 H, s, CH=N); δ_C($CDCl_3$) 110.4 (C-4), 120.8 (q, CF_4, $^1J_{CF}$ 270), 120.9, 124.7, 126.6, 127–129, 137.0 and 151.0 (2 Ph), 138.4 (C-5), 141.9 (q, C-3, $^2J_{CF}$ 38) and 149.1 (CH=N); *m/z* 356 ($M^{\bullet+}$, 6%), 328 ($M^{\bullet+} - N_2$, 47) and 77 (Ph^+, 100).

This compound thermolysed to 5-anilino-4-cyano-1-phenyl-3-trifluoromethylpyrazole; yield 43%, m.p. 149 °C (from *n*-hexane–Et_2O) (Found: C, 62.4; H, 3.5. $C_{17}H_{11}F_3N_4$ requires C, 62.20; H, 3.38%); ν_{max}(KBr)/cm^{-1} 3300s (NH) and 2230s (CN); δ_H($CDCl_3$) 6.15 (1 H, br s, NH), 7.03, 7.15, 7.33 and 7.46–7.54 (10 H, d + 2 t + m, 2 Ph); δ_C($CDCl_3$) 78.8 (C-4), 110.3 (CN), 119.7 (q, CF_3), 120.7, 124.8, 125.3, 129.6, 130.0, 130.1, 136.2 and 137.9 (2 Ph), 143.7 (q, C-3) and 147.9 (C-5); *m/z* 328 ($M^{\bullet+}$, 100%).

5-Azido-3-methoxycarbonyl-1-phenyl-4-(N-phenyliminomethyl)pyrazole **1l**.—Prepared from the corresponding azido aldehyde in 51% yield, m.p. 128 °C (from EtOH) (Found: C, 62.5; H, 4.2. $C_{18}H_{14}N_6O_2$ requires C, 62.43; H, 4.08%); ν_{max}(KBr)/cm^{-1} 2150s (N_3), 1730s (CO) and 1620m (C=N); δ_H($CDCl_3$) 3.95 (3 H, s, MeO), 7.2–7.55 and 7.65 (10 H, 3 m + d, 2 Ph) and 9.15 (1 H, s, CH=N); δ_C($CDCl_3$) 52.3 (MeO), 114.0 (C-4), 121.1, 124.9, 126.3, 128.95, 129.0, 129.1, 137.3 and 151.3 (2 Ph), 138.1 (C-5), 141.9 (C-3), 152.2 (CH=N, $^1J_{CH}$ 168) and 162.2 (CO); *m/z* (no $M^{\bullet+}$), 318 ($M^{\bullet+} - N_2$, 100%).

This compound thermolysed to 5-anilino-4-cyano-3-methoxycarbonyl-1-phenylpyrazole; yield: 57%, m.p. 130 °C (from CCl_4) (Found: C, 67.8; H, 4.3. $C_{18}H_{14}N_4O_2$ requires C, 67.92; H, 4.43%); ν_{max}(KBr)/cm^{-1} 3264m (NH), 2235m (CN) and 1734s (CO); δ_H($CDCl_3$) 3.90 (3 H, s, MeO), 6.85 (1 H, br s, NH), 6.95, 7.00 and 7.2–7.45 (10 H, d + t + m, 2 Ph); δ_C($CDCl_3$) 52.6 (MeO), 83.3 (C-4), 111.8 (CN), 119.1, 123.8, 124.5, 129.3, 129.4, 129.5, 136.5 and 139.1 (2 Ph), 143.6 (C-3), 147.9 (C-5) and 160.4 (CO); *m/z* 318 ($M^{\bullet+}$, 100%).

5-Azido-4-cyano-3-methyl-1-phenylpyrazole **1o**.—Prepared from pyrazole **1a** and hydroxylamine-*O*-sulfonic acid[19] in 73% yield, m.p. 48 °C (from diethyl ether); ν_{max}(KBr)/cm^{-1} 2224s (CN) and 2130s (N_3); δ_H($CDCl_3$) 2.38 (3 H, s, Me), 7.39, 7.46 and 7.53 (5 H, 2 t + d, Ph); δ_C($CDCl_3$) 13.0 (Me), 84.3 (C-4), 111.9 (CN), 123.8, 128.6, 129.2 and 136.8 (Ph), 140.4 (C-5) and 152.3 (C-3); *m/z* 224 ($M^{\bullet+}$, 1%), 196 ($M^{\bullet+} - N_2$, 2) and 49 (100) (Found: $M^{\bullet+}$, 224.0814. $C_{11}H_8N_6$ requires *M*, 224.0810).

This compound thermolysed to α-cyano-β-(phenylazo)-crotononitrile; yield 78%; m.p. 107 °C; ν_{max}(KBr)/cm^{-1} 2230s (CN) and 1591s; δ_H($CDCl_3$) 2.45 (3 H, s, Me), 7.54, 7.63 and 7.99 (5 H, 2 t + d, Ph); δ_C($CDCl_3$) 14.3 (Me), 92.2 and 176.2 (C=C–N), 110.7 and 112.2 (2 CN), 125.0, 129.7, 135.4 and 152.3 (Ph); *m/z* 196 ($M^{\bullet+}$, 4%), 105 (PhN_2^+, 11) and 77 (Ph^+, 100) (Found: $M^{\bullet+}$, 196.0748. $C_{11}H_8N_4$ requires *M*, 196.0749).

5-Azido-4-(2-ethoxycarbonylvinyl)-3-methyl-1-phenylpyrazole **1q**.—Yield 33%; ν_{max}(KBr)/cm^{-1} 2131s (N_3), 1707s (CO) and 1631s (C=C); δ_H($CDCl_3$) 1.35 and 4.26 (5 H, t + q, Et), 2.4 (3 H, s, Me), 6.19 and 7.67 (2 H, d, *J* 16, CH=CH) and 7.38–7.61 (5 H, m, Ph); δ_C($CDCl_3$) 14.1 and 14.3 (Me), 60.4 (CH_2), 108.3 (C-4), 117.2 and 132.4 (C=C), 124.1, 128.3, 129.2 and 137.5 (Ph), 149.3 (C-3) and 167.1 (CO) (C-5 not observed).

This compound thermolysed quantitatively to 2-cyano-4-ethoxycarbonyl-1-methyl-1-phenylazobutadiene and was characterized in solution since it decomposed during the isolation procedure; δ_H($CDCl_3$) 1.4 and 4.3 (5 H, t + q, Et), 2.4 (3 H, s, Me), 6.8 and 7.85 (2 H, 2 d, *J* 16, CH=CH), 7.55–7.65 and 8.05 (5

H, m + d, Ph); $\delta_C(CDCl_3)$ 14.2 and 61.2 (Et), 11.5 (Me), 114.4 (CN), 119.4 (C-2), 124.3, 129.4, 133.4 and 152.6 (Ph), 126.6 (C-4), 135.2 (C-3), 165.1 (C-1) and 165.7 (CO).

5-Azido-3-methyl-4-nitro-1-phenylpyrazole **1r**.—Yield 92%, m.p. 75–76 °C (lit.,[20] 70 °C); ν_{max}(KBr)/cm^{-1} 2169s (N_3), 1550s and 1364s (NO_2); $\delta_H(CDCl_3)$ 2.60 (3 H, s, Me), 7.46, 7.51 and 7.56 (5 H, 2 t + d, Ph); $\delta_C(CDCl_3)$ 14.5 (Me), 124.3, 128.9, 129.0 and 136.6 (Ph), 124.7 (C-4), 136.4 (C-5) and 146.8 (C-3); *m/z* 244 ($M^{\cdot+}$, 0.9%) and 77 (Ph^+, 100).

This compound thermolysed to an intractable black tar which could not be identified. When a tetrachloroethane solution of azide **1r** was thermolysed at 80 °C, the IR spectrum showed peaks at 3488m, 3374m (NH), 2247w and 2224w (CN).

Measurements of Reaction Rates.—Rates were usually measured by the IR method as previously described,[10] the decay of the azido band in the spectrum near 2120 cm^{-1} being monitored. The decompositions of 2-methoxy- and 2-(methylthio)-azidobenzene were not first order unless a free-radical chain inhibitor (2,6-di-*tert*-butyl-4-methylphenol) was used; in this respect these two azides behaved like other simple azidobenzenes.[14] With the azidopyrazoles, the decompositions showed clean first-order kinetics, even as far as three half-lives, in the absence of inhibitor. The inhibitor was added to one of each duplicate pair of kinetic runs, but had no discernible effect on the measured rate constants.

Several rate data (Tables 2 and 6) were obtained by using ^{1}H NMR spectroscopy as the analytical method. Thus, NMR tubes, containing *ca.* 0.25 mol dm^{-3} solutions of the azidopyrazole **1**, were placed in the 250 MHz NMR probe at constant temperature. At measured time intervals, the NMR spectra were analysed by integration of the appropriate signals (H-4 or Me), while the probe temperature was measured with a thermocouple before and after each experiment; readings were within 0.5 °C. The reactions were followed for at least two half-lives and showed linear semilog plots of the concentrations (%) with correlation coefficients of 0.998–0.999.

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