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The Preparation and Thermal Fragmentation of 2-Acyl-5-azidofurans

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Abstract

The reaction of the nitrofurans (1)–(4) with sodium azide in Me_2SO gave the thermally unstable azidofurans (5)–(8), which decompose to give nitrogen and the (*Z*)-dioxoalkenenitriles (32) and (15)–(17) respectively. The azides (6)–(8), the (*Z*)-nitriles (15)–(17) and their (*E*)-isomers (18)–(20) were characterized by spectroscopic techniques. The nitriles were also characterized by formation of Diels–Alder adducts and quinoxaline derivatives. The nitriles (17) and (20) gave the adducts (21a,b) with 2,3-dimethylbuta-1,3-diene, and the nitriles (16) and (19) gave the adducts (23), (24) and (25) (or (26)) with diene (22). The quinoxalines (27)–(31) were prepared by condensation of *o*-phenylenediamine with nitriles (17), (20), (18) and the unstable compounds (32) and (33) respectively. The first-order rate constants for ring-opening of azides (5)–(8) were determined by u.v. spectroscopy in cyclohexane and activation parameters were also evaluated. The trends in activation energies and entropies were rationalized by consideration of valence-bond contributors to the azides and the presumed nitrene intermediates. The acid-catalysed decomposition of azide (5) in methanol was also studied.

As part of a study of the reaction of nitroheteroaromatic compounds, such as nitrothiophens,[1] we prepared the nitrofurans (1)–(4) and treated them with a variety of nucleophiles. There are several reports of substitution of nitro groups in nitrofurans,[2,3] although only one of these refers to substitutions in which the nucleofuge is nitrite ion *and* the activating substituent is an acyl group.[3] In this latter work, the reaction of the nitro aldehyde (1) with sodium azide gave the azidofuran (5), which is reported to be stable for appreciable lengths of time, only at 0–4°. Despite the implication of instability of (5), no decomposition products were reported. We have repeated the reaction of sodium azide with the aldehyde (1), and have additionally studied reaction with the nitro ketones (2)–(4). The resulting azides (5)–(8) undergo facile ring-opening reactions and a preliminary account of these reactions, including approximate rates of decomposition, has been published.[4] This present paper reports

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[1] Newcombe, P. J., and Norris, R. K., *Aust. J. Chem.*, 1982, **35**, 973, and references therein.

[2] Severin, T., and Kullmer, H., *Chem. Ber.*, 1973, **106**, 1688; Doddi, G., Illuminati, G., Mencarelli, P., and Stegel, F., *J. Org. Chem.*, 1976, **41**, 2824; Mencarelli, P., and Stegel, F., *J. Org. Chem.*, 1977, **42**, 3550.

[3] Lieb, F., and Eiter, K., *Justus Liebigs Ann. Chem.*, 1972, **761**, 130.

[4] Newcombe, P. J., and Norris, R. K., *Tetrahedron Lett.*, 1981, 699.

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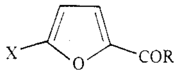
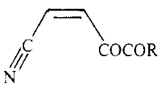
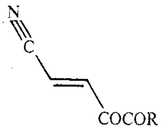
the details and extension of this study, and includes determination of the kinetics and activation parameters for decomposition of the azides (5)–(8).



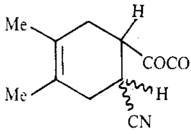
	X	R
(1)	NO_2	H
(2)	NO_2	Me
(3)	NO_2	Pr^i
(4)	NO_2	Bu^t
(5)	N_3	H
(6)	N_3	Me
(7)	N_3	Pr^i
(8)	N_3	Bu^t
(10)	H	Me
(11)	H	Bu^t
(13)	$COBu^t$	Bu^t
(14)	$Ph_3P{=}N$	Me



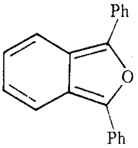
(15) R = Me
(16) R = Pr^i
(17) R = Bu^t
(32) R = H



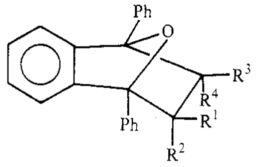
(18) R = Me
(19) R = Pr^i
(20) R = Bu^t
(33) R = H



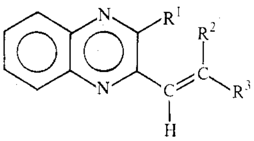
(21a, b)



(22)



	R^1	R^2	R^3	R^4
(23)	H	CN	H	$COCOPr^i$
(24)	CN	H	$COCOPr^i$	H
(25)	H	CN	$COCOPr^i$	H
(26)	CN	H	H	$COCOPr^i$

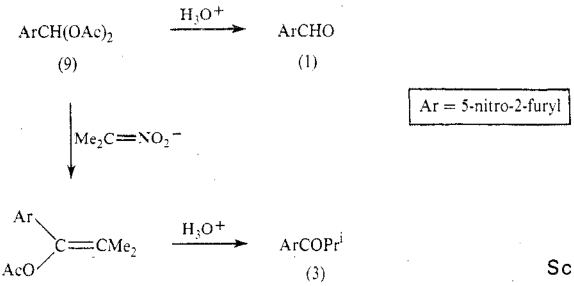


	R^1	R^2	R^3
(27)	Bu^t	CN	H
(28)	Bu^t	H	CN
(29)	Me	H	CN
(30)	H	CN	H
(31)	H	H	CN

Results and Discussion

Preparation of Nitro Compounds (1)–(4)

The aldehyde (1) and the isopropyl ketone (3) were prepared from the commercially available diacetate (9) as outlined in Scheme 1. The ketones (2)[5] and (4) were prepared in the two-step nitration process shown in Scheme 2, from the commercially available ketone (10), and the t-butyl ketone (11) respectively. The ketone (11) was produced in only poor yield on treatment of furan with pivaloyl chloride and tin(IV) chloride.



Scheme 1

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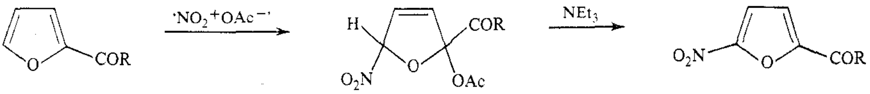
[5] Saldabols, N., and Hillers, S., *Latv. PSR Zinat. Akad. Vestis*, 1958, 101 (*Chem. Abstr.*, 1959, **53**, 11334g).

This method, which has been reported without yield,[6] is an adaption of the high-yielding procedure used in the thiophen system.[7] An excellent yield of (11) could be obtained, however, by reaction of 2-furyllithium (from furan and butyllithium in ether/hexane mixtures[8]) with pivalonitrile. Omission of ether during the preparation of the furyllithium gave only a poor yield of the diketone (13). The addition product (12), in the nitration of ketone (11) (Scheme 2), was very stable, and was isolated and characterized.



(10) R = Me
(11) R = Bu^t

(12) R = Bu^t

Scheme 2

Preparation and Characterization of Azidofurans (5)–(8)

The azide (5) was prepared as previously described.[3] In identical fashion, treatment of nitro ketones (2)–(4) with NaN_3 in Me_2SO gave the azido ketones (6)–(8). Since the ketones decomposed too rapidly for submission of analytical samples and were invariably contaminated with decomposition products (see below), they were characterized by spectroscopic techniques. Each gave strong azide (*c*. 2140 cm^{-1}) and carbonyl (*c*. 1680 cm^{-1}) stretching absorptions in its i.r. spectrum. The u.v. spectra had λ_{max} at 300–310 nm (corrected ε *c*. 16000—see Experimental), and appropriate absorptions in their ^1H n.m.r. spectra for the alkylcarbonyl group and a 2,5-disubstituted furan ($J_{3,4}$ *c*. 3·8 Hz).[9a] Accurate mass measurements confirmed the molecular formulas. The azido ketone (6) was further characterized by preparation of the triphenylphosphine derivative (14).

Characterization of Decomposition Products from Azides (5)–(8)

The crude samples of azides (6)–(8) from the above preparations were each found to contain small amounts (initially 5–15%) of two contaminants, whose proportions increased over several days (at room temperature) until they were the sole species present. The decomposition products were identified as the (*Z*)-dioxoalkenitriles (15)–(17), contaminated with 5–20% of the corresponding (*E*)-isomers (18)–(20). The proportion of (*E*)-isomer increased slowly, on standing. The isomerization was catalysed by triethylamine and by silica gel on attempted chromatography (also accompanied by substantial decomposition) and could be cleanly effected with iodine in benzene or carbon tetrachloride. Since the nitriles (15)–(20) could not be purified by distillation or chromatography their constitutions were confirmed by spectroscopic methods. The *cis* (*J c*. 11·5 Hz) and *trans* (*J c*. 16·5 Hz) 1,2-disubstituted double bonds[9b] and the alkyl substituents were confirmed by ^1H n.m.r. spectroscopy. The carbonyl groups were identified by a strong broad absorption at

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[6] Angelelli, J. M., Katritzky, A. R., Pinzelli, R. F., and Topsom, R. D., *Tetrahedron*, 1972, 2037.

[7] Johnson, J. R., and May, G. E., *Org. Synth.*, 1959, Coll. Vol. II, 8.

[8] Ramanathan, V., and Levine, R., *J. Org. Chem.*, 1962, **27**, 1216.

[9] Jackman, L. M., and Sternhell, S., 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry' 2nd Edn (*a*) p. 306; (*b*) pp. 278, 302; (*c*) p. 289 (Pergamon Press: Oxford 1969).

1700–1710 cm^{-1} in the i.r. spectra, and by ^{13}C spectroscopy (two carbonyl absorptions per molecule at δ *c.* 185 and 204). The nitrile groups only absorbed very weakly in the i.r. spectra, but the appropriate resonances were apparent in the ^{13}C spectra (δ C≡N *c.* 115).

The dioxoalkenenitriles, as a result of their high degree of functionalization, could be readily converted into suitable derivatives. The two routes chosen were formation of Diels–Alder adducts and conversion into quinoxalines.

The mixture of nitriles (17) and (20) readily gave the diastereoisomeric adducts (21a,b) with 2,3-dimethylbuta-1,3-diene. Since these derivatives were inseparable the diene (22) was used, and with the mixture of nitriles (16) and (19) gave three of the four possible adducts (23)–(26). These were readily separated by p.l.c. The constitutions of (23) ($J_{2,3}$ 10·94 Hz $\equiv J_{exo,exo})^{9c}$ and of (24) ($J_{2,3}$ 8·69 Hz $\equiv J_{endo,endo})^{9c}$ could be assigned by ^{1}H n.m.r. spectroscopy. The remaining isomer ($J_{2,3}$ 4·32 Hz $\equiv J_{exo,endo})^{9c}$ could not be unambiguously assigned and is either (25) or (26).

The α-diketone functionality was utilized in condensation with *o*-phenylenediamine. The mixture of dioxo nitriles (17) and (20) gave a readily separable mixture of the quinoxalines (27) and (28), whose stereochemistry was determined by ^{1}H n.m.r. spectroscopy.[9b] In similar fashion the mixture of nitriles (15) and (18) was treated first with iodine in carbon tetrachloride and then with *o*-phenylenediamine to give the (*E*)-quinoxaline (29). Since decomposition of the azido aldehyde (5) gave no discernible, identifiable decomposition products (other than a brown intractable precipitate), by ^{1}H n.m.r. and u.v. spectroscopy (see below), its decomposition in the presence of *o*-phenylenediamine was examined. A moderate yield of the quinoxalines (30) and (31) was obtained. The (*E*)-isomer (31) was stable and was fully characterized. The formation of the derivatives (30) and (31) confirms the formation of the (unstable) nitriles (32) and (33), which can be partly trapped before further alternative and undetermined decomposition reactions take place.

Kinetics of Decomposition of Azides (5)–(8)

The decomposition of the azides (5)–(8) could be conveniently followed by u.v. spectroscopy in the region 300–310 nm, where the ring-opened nitriles (15)–(20) showed negligible absorption (ε *c.* 300) relative to the azides (ε *c.* 16000). First-order rate constants were obtained (see Experimental) and are presented in Table 1. The azido ketones (6)–(8) gave clean conversion into the corresponding nitriles, as confirmed by the occurrence of an isosbestic point in the u.v. traces at *c.* 265 nm, up to 85–90% reaction. Thereafter, the relatively slow decomposition of the products (15)–(20) caused some deviations. The values for the 'infinite time' absorbance (A_∞) required for first-order kinetic analysis (see Experimental) were consequently not directly obtainable and were estimated by extrapolation. These extrapolated values may lead to some systematic errors which are most probably, however, within the reproducibility errors quoted in Table 1. The u.v. traces from the decomposition reactions of the azido aldehyde (5) did not show an isosbestic point, nor were significant absorptions from products observed. These observations confirm the high instability of the nitriles (32) and (33). Since poorly reproducible results were obtained when the dilute solutions of the azides (5)–(8), particularly (5), were exposed to light all stock solutions were kept in flasks wrapped in aluminium foil. Another surprising phenomenon, particularly with the azide (7), was that its decomposition in frozen cyclohexane and/or its decomposition induced by freezing and thawing its solutions in cyclohexane was accelerated beyond that found for solutions kept at 50°! The freshly prepared compound (7) (and the other azides) could be stored, however, *without* significant decomposition in *absence* of solvent for several months at −20°. The ring-opening reactions were examined over a limited temperature range (20–50°) in cyclohexane (Table 1) and the variation in rate constants with temperature allowed determination of the appropriate Arrhenius and Eyring activation parameters (see Table 2).

Table 1. Rate constants for the ring-opening reactions of the azidofurans (5)–(8)

The first-order rate constants were determined by u.v. spectroscopy (see Experimental) and are for cyclohexane solutions unless otherwise stated

Azide	Temp.[A]	10^6k (s^{-1})	Azide	Temp.[A]	10^6k (s^{-1})
(5)	20·0°	1·7±0·1	(7)	20·0°	4·9±0·1
(5)	30·0	10·0±0·7	(7)	30·0	23±3
(5)	40·0	37±3	(7)	40·0	83±5
(5)	50·0	115±15	(7)	50·0	250±10
(5)[B]	20·0	1·6±0·2	(8)	20·0	8·15±0·15
(5)[C]	20·0	9·0±0·3	(8)	30·0	31±2
(5)[D]	20·0	>25000	(8)	40·0	118±5
(6)	20·0	4·4±0·1	(8)	50·0	368±5
(6)	35·0	35±1	(8)[B]	20·0	7·1±0·1
(6)	50·0	245±10	(8)[C]	20·0	4·7±0·1
(6)[C]	20·0	2·4±0·1	(8)[D]	20·0	5·0±0·1
(6)[D]	20·0	9·5±0·3			

[A] ±0·1°. [B] In $CHCl_3$. [C] In CH_3OH. [D] In 0·033 M H_2SO_4 in CH_3OH.

Table 2. Activation parameters for the ring-opening reactions of azidofurans (5)–(8) in cyclohexane

The energy of activation (E_a) and log A were obtained by linear regression analysis of the appropriate data in Table 1, and the Arrhenius equation, and $\Delta S^{\ddagger}$ was obtained in similar fashion from the Eyring equation (see Experimental)

Azide	E_a (kJ mol^{-1})	log A	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	Azide	E_a (kJ mol^{-1})	log A	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
(5)	110±6	14 ±1	12±19	(7)	106±4	13·5±0·7	0±11
(6)	105±1	13·4±0·2	3± 3	(8)	100±1	12·8±0·2	−8± 4

Although the errors involved are substantial (particularly those for log A and $\Delta S^{\ddagger}$, on account of the small temperature range), two general trends are discernible. The energy of activation decreases and the entropy of activation also decreases as the substituent on the carbonyl group is changed from H to Bu^t. The combination of these trends produced the significant differences in half-lives for the series (5)–(8), which, in cyclohexane at 20°, vary from 113 h for (5), through 44 and 39 h for (6) and (7) to 24 h for (8).*

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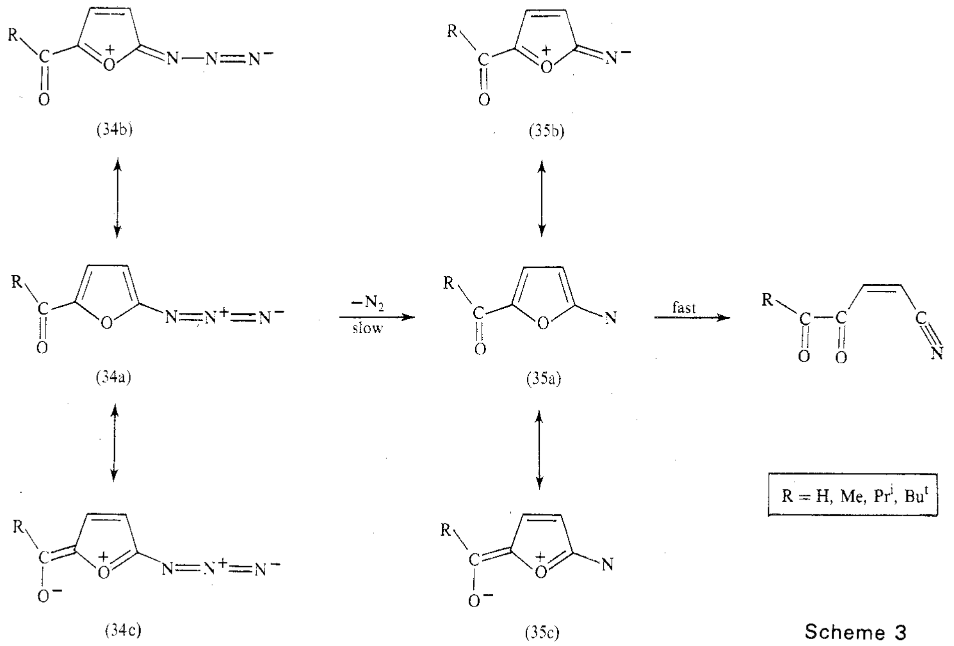
* The *approximate* values originally reported[4] for three of these azides, were determined by ^1H n.m.r. spectroscopy in $CDCl_3$ for solutions kept at 20° but with spectra run at 28–32°. This temperature elevation during recording of spectra, the unrecognized effect of light in catalysing the decomposition of the azides, and the failure of azide (5) to give identifiable products account for the significant differences in half-lives originally reported[4] to those determined in this work.

A possible explanation for the parallel trends in energy and entropy of activation may be found in the following valence-bond argument, which is an expansion of that previously advanced.[4]

The mechanism for the decomposition of azides (5)–(8) is given in Scheme 3 and is analogous with that previously advanced for the vacuum pyrolyses of the isoelectronic diazo(2-furyl)- and diazo(isoxazo-5-yl)-methanes.[10]



Scheme 3

It can be assumed that the overall ring-opening reaction of the azides (5)–(8) involves the transformation (34) → (35) (see Scheme 3) as the rate-determining step and that the transition state leading to (35) is similar in nature to (35). The nitrene intermediate (35) will be significantly stabilized by contribution from (35b) in which donation of electron density from the furan oxygen to the electron-deficient nitrogen takes place. The analogous form (34b) in the starting material will be less significant since it produces disruption of resonance in the azide group, i.e. prevents the resonance:

$$\text{Ar–N=N}^{+}\text{=N}^{-} \leftrightarrow \text{Ar–N}^{-}\text{–N}^{+}\equiv\text{N}$$

Significant contribution from (35c), on the other hand, will reduce the contribution from (35b) and destabilize (35), but increased contribution from (34c) will stabilize (34). Consequently R groups which cause an increase in the importance of contribution from forms (34c) and (35c) will stabilize (34) and destabilize (35); this will lead to a larger energy difference between (34) and (35) than that occurring when R decreases the importance of (34c) and (35c).

In a related fashion, the degree of double-bond character between the carbon of the furan ring and the carbon of the carbonyl group should also show variations with

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[10] Hoffman, R. V., Orphanides, G. G., and Shechter, H., *J. Am. Chem. Soc.*, 1978, **100**, 7927; Hayashi, S. I., Nair, M., Houser, D. J., and Shechter, H., *Tetrahedron Lett.*, 1979, 2961.

the nature of R. In general the amount of double bond character in the above bond should decrease in going from (34) to (35) in response to the greater importance of (35b) than (34b) in the respective species. The *change* in double bond character will be greater, however, when R is a group which causes a relative increase in the importance of contribution from (34c). The change in degree of freedom of rotation about the C (furan) to C (carbonyl) bond and, consequently, the value of $\Delta S^{\ddagger}$, should be larger when R favours form (34c).

The change of R from H through Me and Pr^i to Bu^t can be expected to have both steric and electronic effects. In the preliminary account of this work[4] only the steric effect (i.e. an assumed increase in departure from coplanarity of the acyl group with the furan ring in going from R = H to R = Bu^t) was invoked to explain the decrease in half-lives in the series (5)–(8). Recent results from studies, which were undertaken, in part, because of this predicted increase in noncoplanarity as the size of R is increased, have not in fact convincingly supported the argument concerning steric inhibition of resonance. Kerr effect* measurements have shown that the t-butylcarbonyl group in the model t-butyl ketone (11) does not deviate by more than 20° from coplanarity with the furan ring. This contrasts with a corresponding deviation from coplanarity of 53° in pivalophenone,[11] whose chemistry reflects this effect.[12]

The alternative electronic argument, which does not depend on the above sterically induced inhibition of resonance, is that the field-effect (inductive) electron donation of R groups increases[13a] from H, through Me and Pr^i to Bu^t, and consequently the proportion of contributions from (34c) to (34) and of (35c) to (35) decrease in the same order. This effect is supported quantitatively by values for the appropriate[13b,14] Hammett constant, σ_p^-. The value of σ_p^- for CHO and COMe groups (the others have not been determined) are 1·13 and 0·87.

The operation of both or either of the above phenomena will account for the reduction in E_a on going from (5) to (8). The change in rotational freedom around the C (furan) to C (carbonyl) bond will be greater in (5), for which (34c) is more important, than in (8). This is in accord with the observed trend in $\log A$ and $\Delta S^{\ddagger}$ (Table 2).

The effect of solvent on the decomposition of azides (5)–(8) was only examined superficially. The change from cyclohexane to chloroform (see Table 1) gave a reduction in rate for (5) and (8) of *c.* 10%. By way of contrast, the change from cyclohexane to methanol produced a fivefold rate increase with (5), but with (6) and (8) gave a reduction in rate ($k_{MeOH}/k_{C_6H_{12}} = 0{\cdot}55$ and $0{\cdot}58$ respectively). The addition of dilute acid had an even more dramatic effect. The decomposition of the azido aldehyde (5) was complete in less than 2 min (an increase in rate, relative to that in methanol alone, approaching 3000-fold), whereas the azido ketones (6) and (8) showed increases in rate of only fourfold and 6% respectively. Clearly some specific acid-catalysed process is occurring with the aldehyde (5). The possibility that the aldehyde (5) was decomposing by a different route giving quite different products,

* We thank Dr G. L. D. Ritchie and Mr D. Mirarchi, School of Chemistry, University of Sydney for this result.

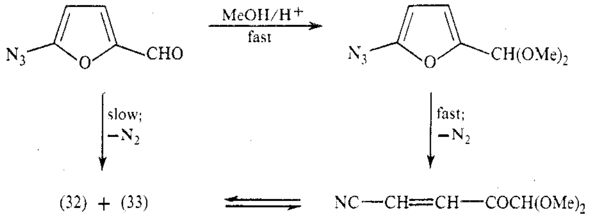
[11] Barker, S. D., Mirarchi, D., Norris, R. K., Phillips, L., and Ritchie, G. L. D., *J. Mol. Struct.*, 1981, **75**, 265.

[12] Barker, S. D., Norris, R. K., and Randles, D., *Aust. J. Chem.*, 1981, **34**, 1875.

[13] March, J., 'Advanced Organic Chemistry: Reactions, Mechanism and Structure' 2nd Edn (*a*) p. 21; (*b*) p. 253; (McGraw–Hill: New York 1977).

[14] Jaffé, H. H., *Chem. Rev.*, 1953, **53**, 191.

rather than nitriles (32) and (33), was removed by treatment of (5) with 0·1 M sulfuric acid in methanol for 1 min at room temperature followed by addition of *o*-phenylenediamine. The quinoxalines (30) and (31) (*c.* 20%) were formed. The yield of (30) and (31) obtained in the absence of strong acid was 50–60% (see Experimental). The possibility of specific reaction of the acid with the azide group is clearly ruled out by absence of catalysis in the reaction with (8). A ready explanation, consistent with the above observations, involves acetal formation, as shown in Scheme 4. The conversion of the formyl group into a dimethoxymethyl group removes contributors analogous with (34c) and (35c) (Scheme 3) *completely* from consideration and leads to a prediction of substantial rate enhancement. This is clearly verified in practice.



Scheme 4

Experimental

Melting points were determined on a Kofler melting point apparatus and are uncorrected. ^1H n.m.r. spectra were determined on a Varian Associates HA100 spectrometer or a Jeol FX60Q spectrometer, with $SiMe_4$ as internal standard on 10% w/v solutions in $CDCl_3$. ^{13}C n.m.r. spectra were recorded on a Jeol FX60Q spectrometer with $SiMe_4$ as internal standard on 10–25% w/v solutions in $CDCl_3$. Multiplicities refer to the off-resonance spectra unless 'fully coupled' is specified. I.r. spectra were recorded on a Perkin–Elmer 221 spectrophotometer and u.v. spectra on a Perkin–Elmer 402 spectrophotometer. Mass spectra were recorded on an A.E.I. MS9 spectrometer at 70 eV. Light petroleum refers to the fraction of b.p. 60–65°. Preparative-layer chromatography (p.l.c.) was performed on Merck Kieselgel 60 $PF_{254+366}$. Thin-layer chromatography (t.l.c.) was performed on Merck Kieselgel $HF_{254+366}$ (type 60). Analyses were carried out at the Australian Microanalytical Service, Melbourne.

Preparation of Nitro Compounds (1)–(4)

(i) *5-Nitrofurfural* (*1*)

Commercially available 5-nitrofurfurylidene diacetate (9) was hydrolysed[15] to give a 70% yield of aldehyde (1), b.p. 153–155°/24 mm (lit.[15] 128–132°/10 mm).

(ii) *1-(5′-Nitro-2′-furyl)ethanone* (*2*)

Acetylfuran was nitrated by a modified version of the literature procedure[5] (see (iv) below), wherein triethylamine replaced pyridine in the elimination step. The ketone (2), m.p. 76–77° (lit.[5] 77–78°), was obtained in 30% yield.

(iii) *2-Methyl-1-(5′-nitro-2′-furyl)propan-1-one* (*3*)

2-Methyl-1-(5′-nitro-2′-furyl)prop-1-enyl acetate was prepared in 50–60% yield from the diacetate (9) and lithium 2-nitropropan-2-ide according to the literature procedure[16] (except that use of

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[15] Gilman, H., and Wright, G. F., *J. Am. Chem. Soc.*, 1930, **52**, 2550.

[16] Freeman, D. J., Newcombe, P. J., and Norris, R. K., *Aust. J. Chem.*, 1976, **29**, 327.

3 equiv. of the lithium salt reduced the reaction time from 3 days to 1 day). The resulting enol acetate (4·5 g, 20 mmol) was dissolved in methanol (75 ml) saturated with hydrogen chloride. The mixture was stirred for 1 h at room temperature and then poured onto ice. The resulting precipitate was filtered off, washed with water, dried and recrystallized from cyclohexane to give *2-methyl-1-(5′-nitro-2′-furyl)propan-1-one* (3) (1·9 g, 52%), white needles, m.p. 53–54° (Found: C, 52·9; H, 5·1; N, 8·0. $C_8H_9NO_4$ requires C, 52·5; H, 5·0; N, 7·7%). ^{1}H n.m.r.: δ 1·26, d, J 6·87 Hz, $CHMe_2$; 3·43, sept, J 6·87 Hz, H2; 7·27, d, J 3·81 Hz, H3′; 7·37, d, J 3·81 Hz, H4′. ν_{max} (chloroform) 1690, 1535, 1370, 1265, 1025 cm^{-1}. λ_{max} (methanol) 222 (ε 7900), 303 nm (20100). *m/z* 183 (M, 35%), 168 (11), 141 (43), 140 (26), 124 (39), 96 (17), 94 (15), 66 (20), 43 (100), 41 (40), 39 (22), 38 (27).

(iv) *2,2-Dimethyl-1-(5′-nitro-2′-furyl)propan-1-one* (*4*)

(A) *1-(2′-Furyl)-2,2-dimethylpropan-1-one* (*11*).—Butyllithium (1·6 M in hexane, 150 ml, 0·24 mol) was added to ether (150 ml) at −20° and furan (17·1 g, 0·25 mol) was added. The solution was allowed to warm to room temperature and was then heated under reflux for 4 h.[8] Pivalonitrile (21·2 g, 0·25 mol) was added and the solution was allowed to stand at room temperature overnight. The reaction mixture was poured onto 3 M hydrochloric acid (300 ml) and stirred for 3 days. The mixture was worked up by extraction with ether; the combined ether layers were washed with water, 10% sodium hydrogencarbonate, brine and were dried ($MgSO_4$). Evaporation of the solvent followed by distillation gave 1-(2′-furyl)-2,2-dimethylpropan-1-one (11) (35·0 g, 95%), b.p. 93–94°/25 mm (lit.[6] 56°/2 mm). When the reaction was performed without the initial dilution with ether a white insoluble residue formed which did not dissolve on subsequent dilution with ether or after prolonged reflux (4 h). Proceeding with the reaction as above gave, after workup and recrystallization from chloroform/light petroleum, white crystals of *1,1′-(furan-2″,5″-diyl)bis(2,2-dimethylpropan-1-one)* (13) (16·4 g, 29%), m.p. 124·5–125·5° (Found: C, 70·8; H, 8·7. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%). ^{1}H n.m.r.: δ 1·40, s, CMe_3; 7·20, s, H3″ and H4″. ^{13}C n.m.r. (fully coupled spectrum): δ 26·4, q sept, $^1J_{C,H}$ 128, $^3J(C,Me_2)$ 4 Hz, C3; 43·0, dectet, $^2J(C,Me_3)$ 5 Hz, C2; 118·3, dd, $^1J_{C,H}$ 181 Hz, $^2J_{C,H}$ 4 Hz, C3″ and C4″; 152·6, t, $^2J_{C,H}+{}^3J_{C,H}$ 16 Hz, C2″ and C5″; 194·8, m, $^2J(C,Me_3)$ 5 Hz, C1. ν_{max} (chloroform) 1670, 1005, 925 cm^{-1}. λ_{max} (ethanol) 220 (ε 8800), 288 nm (23900). *m/z* 237 (M+1, 1%), 236 (M, 9), 180 (35), 152 (18), 110 (18), 57 (100), 41 (28).

(B) *Nitration of ketone* (*11*).—The ketone (11) (20·0 g) in acetic anhydride (30 ml) was added dropwise to a prepared (at 0–10°) solution of acetic anhydride (133 ml), conc. nitric acid (13·8 ml) and fuming nitric acid (0·8 ml), over 30 min at −10°. The solution was stirred at −10° for a further 30 min, then allowed to warm to room temperature, poured onto ice, and pyridine (3 drops) was added to catalyse the decomposition of the acetic anhydride. After 3 h at 0–10° the reaction mixture was extracted with ether (*without* the usual[5] neutralization to pH 5·5) and the ether extracts were washed with water, sodium hydrogencarbonate (10%) and brine, and then dried ($MgSO_4$). Removal of the solvent gave a thick oil containing white crystals. Recrystallization of a small sample from ethanol gave *2-(2′,2′-dimethyl-1′-oxopropyl)-5-nitro-2,5-dihydrofuran-2-yl acetate*, white needles, m.p. 128–129·5 (Found: C, 51·6; H, 5·9; N, 5·3. $C_{11}H_{15}NO_6$ requires C, 51·4; H, 5·9; N, 5·4%). ^{1}H n.m.r.: δ 1·21, s, CMe_3; 2·10, s, Me; 6·24–6·46, m, H2,3,4. ^{13}C n.m.r.: δ 20·5, MeCO; 27·0, CMe_3; 45·3, CMe_3; 110·0, C5; 112·5, C2; 128·3 and 136·0, C3 and C4; 168·4, MeCOO; 204·8, CO. ν_{max} (chloroform) 1760, 1710, 1575, 1475, 1415, 1100, 955, 925, 855 cm^{-1}. λ_{max} (ethanol) 215 (ε 2760), 295 nm (235).

The majority of the crude sample from above was dissolved in chlofororm (40 ml) and was treated with triethylamine (15·0 g) in ether (150 ml). After 15 min the reaction mixture was washed with 1 M hydrochloric acid, water, 10% sodium hydrogencarbonate and brine and dried ($MgSO_4$); the solvent was evaporated. Recrystallization of the crude product from methanol and then light petroleum gave *2,2-dimethyl-1-(5′-nitro-2′-furyl)propan-1-one* (4) (13·7 g, 53%), yellow prisms, m.p. 100·5–101° (Found: C, 54·9; H, 5·8; N, 7·0. $C_9H_{11}NO_4$ requires C, 54·8; H, 5·6; N, 7·1%). ^{1}H n.m.r.: δ 1·40, s, Me_3; 7·26, d, and 7·35, d, AB quartet, J 3·84 Hz, H3′ and H4′. ^{13}C n.m.r. (coupled spectrum): δ 26·3, q sept, $^1J_{C,H}$ 128 and $^3J(C,Me_2)$ 4 Hz, CMe_3; 43·6, dectet, $^2J(C,Me_3)$ 4 Hz, C2; 111·5, dd, $^1J_{C,H}$ 189 and $^2J_{C,H3'}$ 4 Hz, C4′; 118·7, d, $^1J_{C,H}$ 186 Hz, C3′; 151·3, t, $^2J_{C,H3'}+{}^3J_{C,H4'}$ 16 Hz, C2′; 194·4, m, C1. ν_{max} (chloroform) 1680, 1530, 1375, 1185, 910 cm^{-1}. λ_{max} (methanol) 302 (ε 15700) nm. *m/z* 197 (M, 9%), 141 (54), 124 (12), 57 (100), 41 (38), 39 (11), 29 (31).

Preparation of Azides (5)–(8)

The appropriate nitro compound (1·6–2·2 mmol) and sodium azide (5·0 mmol) were allowed to react in Me_2SO (10 ml) until the reaction was complete (by t.l.c.). The reaction mixtures were worked up by dilution with ice-water, followed by extraction into ether. The ether extracts were washed thoroughly with cold water and brine, dried ($MgSO_4$) and the solvent was evaporated at *room temperature* under reduced pressure. The crude products were purified or characterized as indicated below. The crude yields of (7) and (8) were estimated by ^{1}H n.m.r. with 2,4,6-trinitrotoluene as internal standard. U.v. data for (6)–(8) have an uncertainty of $\pm 5\%$ in ε values, which were corrected for impurities present.

(i) *5-Azidofurfural* (*5*)

The residue from the reaction of (1) with sodium azide for 30 min after removal of the ether was recrystallized rapidly from light petroleum to yield 5-azido-2-furaldehyde (5) (0·30 g, 55%), pale yellow prisms, m.p. 56–57° (lit.[3] 56–57°). ^{1}H n.m.r.: δ 6·00, dd, J 3·75 and 0·20 Hz, H4; 7·27, d, J 3·75 Hz, H3; 9·44, d, J 0·20 Hz, CHO. ^{13}C n.m.r.: δ 97·6, d, C4; 125·2, d, C3; 148·6, s, and 150·6, s, C2 and C5; 175·4, d, CHO. ν_{max} (chloroform) 2150, 1680, 1585, 1500, 1050 cm^{-1}. λ_{max} ($CHCl_3$) 321 nm (ε 16100); (cyclohexane) 311 nm (15900). m/z 137 (M, 8%), 80 (90), 42 (100), 29 (50), 28 (90).

(ii) *1-(5′-Azido-2′-furyl)ethanone* (*6*)

The crude product from the reaction of (2) with sodium azide for 2 h was rapidly recrystallized from light petroleum (b.p. 30–40°) to give the *azido ketone* (6) (50–55%), yellow crystals, m.p. 69–72° (high-resolution mass spectrum: M$^{+\cdot}$, 151·0369. $C_6H_5N_3O_2$ requires M$^{+\cdot}$, 151·0381). ^{1}H n.m.r.: δ 2·40, s, Me; 5·84, d, $J_{3,4}$ 3·83 Hz, H4′; 7·09, d, $J_{3,4}$ 3·83 Hz, H3′. ^{13}C n.m.r.: δ 25·5, s, Me; 97·3, d, C4′; 120·8, d, C3′; 148·4 s and 148·7 s, C2′ and 5′; 184·6 s, CO. ν_{max} ($CHCl_3$) 2145, 1670, 1495, 1040 cm^{-1}. λ_{max} (cyclohexane) 302 nm (ε 15900). m/z 151 (M, 2·5%), 81 (10), 80 (15), 52 (24), 43 (100), 28 (50). The azide (6) (0·21 g, 1·4 mmol) was characterized further by reaction with triphenylphosphine (0·36 g, 1·4 mmol) in benzene (2 ml) at 10° for 1·5 h. The crystalline product was recrystallized from benzene to give tan crystals, m.p. 152–153°, of *1-[5′-(triphenylphosphoranediylamino)-2′-furyl]ethanone* (14) (0·39 g, 72%) (Found: C, 75·3; H, 5·3; N, 3·0. $C_{24}H_{20}NO_2P$ requires C, 74·8; H, 5·2; N, 3·6%). (High-resolution mass spectrum: M$^{+\cdot}$, 385·1222. $C_{24}H_{20}NO_2P$ requires M$^{+\cdot}$, 385·1231.) ^{1}H n.m.r.: 2·11, s, Me; 5·12, dd, $J_{3',4'}$ 3·6 Hz, $J_{3',P}$ 0·9 Hz, H3′; 7·08, dd, $J_{3',4'}$ 3·6, $J_{4',P}$ 1·8 Hz, H4′; 7·3–7·8, m, 3 × Ph. ν_{max} (chloroform) 1630, 1590, 1470, 1140, 940 cm^{-1}. λ_{max} (ethanol) 210 (ε 35500), 225sh (26200), 375 nm (26000). m/z 385 (M, 61%), 262 (100), 183 (71), 108 (45), 77 (4), 43 (9).

(iii) *2-Methyl-1-(5′-azido-2′-furyl)propan-1-one* (*7*)

The crude product (estimated yield *c.* 84%), from reaction of (3) with sodium azide for 6 h, was dissolved in light petroleum at 25°, the solution was filtered and cooled to −10°. The resulting sample of the *azide* (7) had m.p. 38–39°, but liquefied at 20° on standing at room temperature for several hours (partial decomposition) (high-resolution mass spectrum: M$^{+\cdot}$, 179·0694. $C_8H_9N_3O_2$ requires M$^{+\cdot}$, 179·0686). ^{1}H n.m.r.: δ 1·19, d, J 6·84 Hz, **Me**$_2$CH; 3·22, sept, J 6·84 Hz, H2; 5·91, d, J 3·76 Hz, H4′; 7·18, d, J 3·76 Hz, H3′. ^{13}C n.m.r. (coupled spectrum): δ 18·7, qquin, $^1J_{C,H}$ 127 and $^3J_{C,Me} \approx {}^2J_{C,H2}$ 5 Hz, Me_2; 35·7, dsept, $^1J_{C,H}$ 125 and $^2J(C,Me_2)$ 4 Hz, C2; 96·9, dd, $^1J_{C\ H}$ 182 and $^2J_{C,H3'}$ 4 Hz, C4′; 120·2, dd, $^1J_{C,H}$ 178 and $^2J_{C,H4'}$ 3 Hz, C3′; 147·7, d, ^2J 8 Hz, and 148·3, ^2J 8 Hz, C2′ and C5′; 191·5, m, C1. ν_{max} (chloroform) 2140, 1660, 1590, 1495, 1410, 1375, 1040, 1025 cm^{-1}. λ_{max} (cyclohexane) 303 nm (ε 15900). m/z 179 (M, 3%), 81 (42), 80 (30), 71 (70), 53 (55), 52 (59), 43 (100), 41 (74), 28 (83).

(iv) *2,2-Dimethyl-1-(5′-azido-2′-furyl)propan-1-one* (*8*)

The crude product (estimated yield *c.* 65%), from reaction of (4) with sodium azide for 12 h, gave the *azide* (8), as an orange oil contaminated with 5–10% of nitrile (17), see below. (High-resolution mass spectrum: M$^{+\cdot}$, 193·0852. $C_9H_{11}N_3O_2$ requires M$^{+\cdot}$, 193·0851.) ^{1}H n.m.r.: δ 1·35, s, Me_3; 5·90, d, J 3·81 Hz, H4′; 7·20, d, J 3·81 Hz, H3′. ^{13}C n.m.r.: δ 26·7, q, Me_3; 42·4, s, C2; 96·7, d, C4′; 121·2, d, C3′; 147·1, s, and 147·4, s, C2′ and C5′. ν_{max} (liquid film)

2145, 1680, 1530, 1490, 910 cm^{-1}. λ_{max} (chloroform) 311 nm (ε 15200). *m/z* 193 (M, 0·2%), 141 (2), 85 (12), 81 (20), 81 (13), 57 (100), 41 (72), 29 (56), 28 (43).

Decomposition of Azides (5)–(8) and Identification of Nitriles (15)–(20), (32) and (33)

The azides (6)–(8), on standing in solution or in absence of solvent at room temperature for 5–15 days or on reflux in a solvent, were converted into the corresponding ring-opened products. Since these products decomposed and isomerized on distillation and chromatography the following spectroscopic data were obtained, and the appropriate derivatives below were prepared.

Nitrile (15) and (18) from Azide (6)

(Z)-*4,5-Dioxohex-2-enenitrile* (15): ^{1}H n.m.r. δ 2·43, s, Me; 6·04, d, $J_{2,3}$ 11·6 Hz, H2; 7·65, d, $J_{2,3}$ 11·6 Hz, H3. ^{13}C n.m.r. δ 23·5, q, Me; 111·5, d, C2; 114·9, s, C1; 136·9, d, C3; 183·3, s, C4; 196·0, s, C5.

(E)-*4,5-Dioxohex-2-enenitrile* (18): ^{1}H n.m.r. δ 2·41, s, Me; 6·58, d, $J_{2,3}$ 16·4 Hz, H2; 7·65, d, $J_{2,3}$ 16·4 Hz, H3. ^{13}C n.m.r. δ 23·8, q, Me; 114·1, d, C2; 115·8, s, C1; 138·0, d, C3; 182·8, s, C4; 196·2, s, C5. I.r. ($CHCl_3$—mixture of isomers) ν_{max} 2240 (weak), 1725, 1710 cm^{-1}.

Quinoxaline Derivative (29)

The (*E*)-isomer (18), prepared by heating the azide (6) (200 mg) in CCl_4 (3 ml) with iodine (20 mg) for 5 h, followed by evaporation of solvent, was treated with *o*-phenylenediamine (160 mg), 3 M HCl (0·5 ml) in ethanol (3 ml) for 1 h. The reaction mixture was worked up by dilution with 10% sodium hydrogencarbonate (15 ml) followed by extraction with ether in the usual fashion to give (E)-*3-(3′-methylquinoxalin-2′-yl)prop-2-enenitrile* (29) (180 mg, 70%), tan crystals, m.p. 149–150° (Found: C, 73·9; H, 4·7; N, 21·6. $C_{12}H_9N_3$ requires C, 73·8; H, 4·7; N, 21·5%). ^{1}H n.m.r.: 2·83, s, Me; 6·81, d, $J_{2,3}$ 15·8 Hz, H2; 7·76, d, $J_{2,3}$ 15·8 Hz, H3; 7·6–8·1, m, 4×aryl H. ^{13}C n.m.r.: δ 22·3, q, Me; 104·7, d, H2; 128·7, 129·6, 129·8, 131·0, each d, C5′,6′,7′ and 8′; 141·2, 143·0, 145·2, each s, C3′,4a′,8a′; 143·8, d, C3; 152·1, s, C2′. ν_{max} ($CHCl_3$) 2240, 1560, 1480, 975 cm^{-1}. λ_{max} (ethanol) 210 (ε 19000), 265 (25100), 337 nm (11400). *m/z* 195 (M, 77%), 117 (100), 76 (61), 50 (36).

Nitriles (16) and (19) from Azide (7)

(Z)- and (E)-*6-Methyl-4,5-dioxohept-2-enenitriles* (16) and (19): ^{1}H n.m.r. δ 1·15, d, J 6·84 Hz, Me_2; 3·49, sept, J 6·84 Hz, H6; ((*Z*)-isomer) 6·09, d, J 11·62 Hz, H2; 7·66, d, J 11·62 Hz, H3; ((*E*)-isomer) 6·54, d, J 16·41 Hz, H2; 7·66, d, J 16·41 Hz, H3. ^{13}C n.m.r. (coupled spectrum) δ 17·2, qquin, $^1J_{C,H}$ 128 and $^3J_{C,Me} \approx {}^2J_{C,H6}$ 5 Hz, Me_2; 33·8, dsept, $^1J_{C,H}$ 126 and $^2J(C,Me_2)$ 4 Hz, C6; ((*Z*)-isomer) 111·2, dd, $^1J_{C,H}$ 174 and $^2J_{C,H3}$ 7 Hz, C2; 115·2, s, C1; 137·5, d, $^1J_{C,H}$ 167 Hz, C3; 184·2, s, C4; 203·3, m, C5; ((*E*)-isomer) 111·0, dd, $^1J_{C,H}$ 190 and $^2J_{C,H3}$ 7 Hz, C2; 137·9, d, $^1J_{C,H}$ 179 Hz, C3. Resonances for carbons C1, C4, and C5 in the (*E*)-isomer (19) could not be unambiguously identified. ν_{max} (liquid film) 2225, 1705, 1600, 1475 cm^{-1}.

Diels–Alder Adducts of the Nitriles (16) and (19) with 1,3-Diphenylisobenzofuran (22)

A mixture of the nitriles (16) and (19) (70 mg, 0·46 mmol) and 1,3-diphenylisobenzofuran[17] (22) (162 mg, 0·60 mmol) were dissolved in dichloromethane (2 ml) and the solution was stirred for 0·5 h at room temperature. The solvent was then removed and the residue was separated into components by p.l.c. to give three isomeric adducts:

(1α,2α,3α,4α)-3-(3′-Methyl-1′,2′-dioxobutyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-expoynaphthalene-2-carbonitrile (24) (21 mg, 11%), a yellow oil (Found: C, 80·0; H, 5·5; N, 2·9. $C_{28}H_{23}NO_3$ requires C, 79·8; H, 5·5; N, 3·3%). ^{1}H n.m.r.: δ 0·71, d, J 7·03 Hz, Me; 1·00, d, J 6·78 Hz, Me; 3·13, br sept, J *c.* 6·9 Hz, H3′; 3·68, d, J 8·69 Hz, H2; 4·86, d, J 8·69 Hz, H3; 7·0–7·9, m, phenyl protons. ν_{max} (chloroform) 2245, 1710, 1660, 1445, 1295, 700 cm^{-1}. λ_{max} (methanol) 253 nm (ε 8600).

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(1α,2β,3α,4α)- or *(1α,2α,3β,4α)-3-(3′-Methyl-1′,2′-dioxobutyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalene-2-carbonitrile* (25) or (26) (57 mg, 29%), yellow prisms (ethyl acetate/light petroleum), m.p. 137–140° (Found: C, 79·8; H, 5·8; N, 3·2. $C_{28}H_{23}NO_3$ requires C, 79·8; H, 5·5; N, 3·3%). ^{1}H n.m.r.: δ 0·37, d, J 7·17 Hz, Me; 0·92, d, J 6·76 Hz, Me; 2·79, br sept, J *c.* 7·0 Hz, H 3′; 4·07, d, J 4·32 Hz, H 2; 4·80, d, J 4·32 Hz, H 3; 7·1–8·0, m, phenyl protons. ν_{max} (chloroform) 2240, 1780, 1710, 1455, 1445, 1005 cm^{-1}. λ_{max} (methanol) 248 nm (ε 9600).

(1α,2β,3β,4α)-3-(3′-Methyl-1′,2′-dioxobutyl)-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalene-2-carbonitrile (23) (86 mg, 44%), a yellow oil (Found: C, 79·8; H, 5·6. $C_{28}H_{23}NO_3$ requires C, 79·8; H, 5·5%). ^{1}H n.m.r. δ 1·03, d, J *c.* 7 Hz, Me; 1·10, d, J *c.* 7 Hz, Me; 3·28, sept, J *c.* 7 Hz, H 3′; 4·16, d, J 10·94 Hz, H 2; 4·72, d, J 10·94 Hz, H 3; 7·1–7·9, m, phenyl protons. ν_{max} (chloroform) 2240, 1710, 1455, 1445, 1005 cm^{-1}. λ_{max} (methanol) 248 nm (ε 10100).

Nitriles (17) and (20) from Azide (8)

(Z)-*6,6-Dimethyl-4,5-dioxohept-2-enenitrile* (17): ^{1}H n.m.r. δ 1·31, s, CMe$_3$; 6·10, d, $J_{2,3}$ 11·7 Hz, H 2; 7·45, d, $J_{2,3}$ 11·7 Hz, H 3. ^{13}C n.m.r. δ 25·7, q, CMe$_3$; 42·4, s, C 6; 110·8, d, C 2; 114·8, s, C 1; 139·3, d, C 3; 185·0, s, C 4; 204·6, s, C 5.

(E)-*6,6-Dimethyl-4,5-dioxohept-2-enenitrile* (20): ^{1}H n.m.r. δ 1·31, s, CMe$_3$; 6·45, d, $J_{2,3}$ 16·7 Hz, H 2; 7·64, d, $J_{2,3}$ 16·7 Hz, H 3. ^{13}C n.m.r. δ 25·7, q, CMe$_3$; 42·4, s, C 6; 113·6, d, C 2; 115·6, s, C 1; 140·3, d, C 3; 185·7, s, C 4; 204·6, s, C 5.

I.r., u.v. and mass spectral data were obtained from an 88 : 12 mixture of (17) and (20): ν_{max} (liquid film) 2225, 1700, 1595, 1475, 910 cm^{-1}. λ_{max} (methanol) 239 (ε 6300), 310 nm (300). *m/z* 165 (M, 0·5%), 149 (2), 99 (17), 85 (7), 80 (9), 57 (100), 41 (44), 39 (12), 29 (30).

Diels–Alder Adducts of the Nitriles (17) and (20) with 2,3-Dimethylbuta-1,3-diene

A mixture of nitriles (17) (88%) and (20) (12%) (50 mg, 0·3 mmol) was dissolved in 2,3-dimethylbuta-1,3-diene (1 ml) and the mixture was warmed at 40° for 0·5 h. Excess diene was removed under vacuum and the residue was purified by p.l.c. on silica gel with 40% benzene/60% light petroleum as the eluent to give an inseparable mixture, of indeterminate isomeric composition, of *3,4-dimethyl-6-(3′,3′-dimethyl-1′,2′-dioxobutyl)cyclohex-3-enecarbonitrile* (21a,b) (65 mg, 88%), a bright yellow oil (Found: C, 72·6; H, 8·7; N, 6·0. $C_{15}H_{21}NO_2$ requires C, 72·8; H, 8·6; N, 5·7%). ^{1}H n.m.r.: δ 1·29, s, Me$_3$; 1·65, br d, 3-Me and 4-Me; 2·28, br d, 4H, H 2 and H 5; 2·9–3·7, H 1 and H 6. ^{13}C n.m.r.: δ 18·3, Me; 18·5, Me; 25·7 and 25·9, Me$_3$; 29·0, 32·1, 33·1 and 33·9, C 2 and C 5; 42·4, C 3′; 42·8 and 44·1, C 1 and C 6; 119·8 and 120·9, CN; 122·7, 123·0, 123·8 and 124·2, C 3 and C 4. Resonances for the carbonyl carbons C 1′ and C 2′ were not detected. ν_{max} (liquid film) 2245, 1705 cm^{-1}. λ_{max} (methanol) 297 nm (ε 800). *m/z* 247 (M, 4%), 219 (6), 134 (6), 108 (21), 107 (12), 93 (7), 57 (100), 41 (14), 39 (4), 29 (9).

Quinoxaline Derivatives of the Nitriles (17) and (20) with o-Phenylenediamine

The mixture of nitriles (17) (88%) and (20) (12%) (0·10 g, 0·60 mmol) was dissolved in ethanol (3 ml). Hydrochloric acid (3 M, 0·5 ml) and powdered *o*-phenylenediamine (0·08 g, 0·7 mmol) were added and the mixture was stirred for 0·2 h at room temperature. Dilute sodium hydrogencarbonate was added to neutralize the mixture and the reaction mixture was worked up by ether extraction in the usual manner. The crude product, a brown oil, was separated into components by p.l.c. to give:

(Z)-*3-(3′-t-Butylquinoxalin-2′-yl)prop-2-enenitrile* (27) (36 mg, 25%), pale yellow needles (light petroleum), m.p. 67–69·5° (Found: C, 75·6; H, 6·3; N, 17·8. $C_{15}H_{15}N_3$ requires C, 75·9; H, 6·4; N, 17·7%). ^{1}H n.m.r.: δ 1·55, s, Me$_3$; 5·82, d, J 11·54 Hz, H 2; 7·88, d, J 11·54 Hz, H 3; 7·7–8·3, m, H 5′,6′,7′,8′. ^{13}C n.m.r.: δ 29·9, q, Me$_3$; 38·4, s, CMe$_3$; 102·3, d, C 2; 116·5, s, C 1; 128·9, 129·7, and 130·8, C 5′, C 6′, C 7′ and C 8′; 139·8 and 140·9, C 4a′, C 3′, and C 8a′; 145·6, d, C 3; 160·7, C 2′. ν_{max} (chloroform) 2225, 1560, 1475, 1080 cm^{-1}. λ_{max} (methanol) 240 (ε 19900), 256 (24200), 325 nm (9800). *m/z* 237 (M, 59%), 236 (19), 222 (100), 197 (28), 181 (19), 103 (35), 76 (27), 57 (25), 41 (19), 29 (18).

(E)-*3-(3′-t-Butylquinoxalin-2′-yl)prop-2-enenitrile* (28) (16 mg, 11%), an oil which crystallized over several days under vacuum into a tan solid, m.p. 86–88° (Found: C, 75·7; H, 6·7; N, 17·2.

$C_{15}H_{15}N_3$ requires C, 75·9; H, 6·4; N, 17·7%). ^{1}H n.m.r.: δ 1·59, s, Me$_3$; 6·82, d, J 15·4 Hz, H2; 7·31, dd, J 5·74 and 3·91 Hz, H8′; 7·7–7·8, m, H5′ and H7′; 7·9–8·0, m, H6′; 8·14, d, J 15·4 Hz, H3. ^{13}C n.m.r.: δ 30·3, q, Me$_3$; 38·5, s, CMe$_3$; 103·5, d, C2; 118·0, s, C1; 129·1, 129·9 and 130·9, each d, C5′, C6′, C7′ and C8′; 140·1, s, C4a′; 144·7, s, C8a′; 146·6, d, C3; 161·0, C2′. ν_{max} (chloroform) 2225, 1475, 1360, 1145, 1085 cm^{-1}. λ_{max} (methanol) 239 (ε 16900), 256 (20200), 325 nm (9800). m/z 237 (M, 46%), 236 (18), 222 (100), 197 (29), 181 (18), 103 (29), 76 (27), 57 (29), 41 (22), 29 (21).

Trapping of Nitriles (32) and (33) from Azide (5)

The azide (5) (200 mg, 1·5 mmol) was heated under reflux with *o*-phenylenediamine (163 mg, 1·7 mmol) in ethanol (6·0 ml) for 1 h. Evaporation of the ethanol followed by examination by ^{1}H n.m.r. spectroscopy showed that the major product was (Z)-*3-(quinoxalin-2′-yl)prop-2-enenitrile* (30). ^{1}H n.m.r.: δ 5·85, d, $J_{2,3}$ 11·9 Hz, H2; 7·39, d, $J_{2,3}$ 11·9 Hz, H3; 7·6–7·9, m, H6′ and 7′; 8·0–8·2, m, H5′ and 8′; 9·14, s, H2′. Attempts to purify (30) by chromatography on silica gel gave the more stable isomer (31). Recrystallization of the chromatographed material gave (E)-*3-(quinoxalin-2′-yl)prop-2-enenitrile* (31) (72 mg, 30%), tan crystals (cyclohexane), m.p. 129–131 (Found: C, 72·9; H, 3·6; N, 23·0. $C_{11}H_7N_3$ requires C, 72·9; H, 3·9; N, 23·2%). ^{1}H n.m.r.: δ 6·73, d, $J_{2,3}$ 16·1 Hz, H2; 7·58, d, $J_{2,3}$ 16·1 Hz, H3; 7·7–8·1, m, H5′,6′,7′ and 8′; 8·83, s, H2′. ^{13}C n.m.r.: δ 103·8, d, C2; 117·2, s, C1; 129·2, 129·8, 131·0, 131·2, each d, C5′,6′,7′ and 8′; 142·0, 143·0, each s, C4a′ and 8a′; 144·3, 145·4, each d, C3 and 3′; 145·9, s, C2′. ν_{max} (chloroform) 2230, 1490, 1155, 980 cm^{-1}. λ_{max} (ethanol) 208 (ε 15700), 258 (30000), 339 nm (10200). m/z 181 (M, 100%), 152 (28), 103 (79), 76 (94), 50 (84).

The crude combined yield of quinoxalines (30) and (31) in the crude reaction product was estimated by ^{1}H n.m.r. and was 50–60%. When the azide in methanol was treated with sulfuric acid (overall concentration *c.* 0·1 M) for one min at room temperature and then with *o*-phenylenediamine at room temperature for 5 min followed by workup as above a combined yield of (30) and (31) of *c.* 20% was obtained.

Determination of Kinetics of Decomposition of Azides (5)–(8)

The rates of decomposition of the azides (5)–(8) in the appropriate solvent (see Table 1) were determined by following the decrease in u.v. absorption at the λ_{max} for the appropriate azide (*c.* 305 nm). The reactions were carried out in stoppered flasks, wrapped in aluminium foil, immersed in the temperature-controlled water-bath of a Colora Kryothermostat WK 5 cooling system maintained at the appropriate temperature (see Table 1). Concentrations were *c.* $4 \cdot 5 \times 10^{-4}$ M, and with a 0·2 cm path length these solutions gave initial absorbances of 1·0–1·5. Samples were removed at appropriate time intervals and absorbance was measured with a Perkin–Elmer 402 spectrophotometer. At higher temperatures the samples in cyclohexane were rapidly cooled to *c.* 10° (*freezing* of the solutions gave *enhanced* decomposition and consequently erroneous results) and were then returned to room temperature before u.v. analysis. The decomposition during sample handling at laboratory temperature (*c.* 20°) was negligible (analysis time $\leqslant$7 min). The values for A_∞, absorbance at 'infinite' time, were obtained by extrapolation of the u.v. traces before departure from isosbestic behaviour and were typically 0·02–0·04. The mean value of 0·03 was used for aldehyde (5). Plots of $\ln(A_t - A_\infty)$against time, where A_t is absorbance at time t, were linear (correlation coefficients $\geqslant$0·998) and the first-order rate constants were determined from the slopes. Reactions were performed in at least duplicate. Activation parameters were calculated from the variable temperature data in Table 1 and the Arrhenius and Eyring equations, eqns (*1*) and (*2*) respectively

$$k = A\exp(E_a/RT) \qquad (1)$$

$$k = (k_BT/h)\exp(\Delta S^\ddagger/R)\exp(-\Delta H^\ddagger/RT) \qquad (2)$$

where k is the rate constant at temperature T, E_a is the energy of activation, and k_B, h and R are Boltzmann, Planck and gas constants respectively. Linear regression analysis of $\ln k$ against $1/T$ was used to calculate the slope, $-E_a/R$, and the intercept, $\ln A$ from eqn (*1*), and the intercept from a plot of

$\ln(k/T)$ against $1/T$ yielded $\Delta S^{\ddagger}$ from eqn (*2*). The correlation coefficients for these plots were $\geqslant 0\cdot997$, and the activation parameters so obtained, are summarized in Table 2.

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