The Reaction of Meldrum's Acid with α-Dicarbonyl Monohydrazones: A New Synthesis of Pyridazin-3-ones

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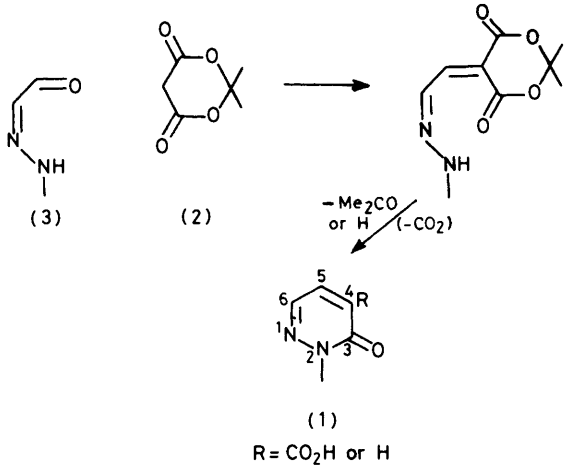
Treatment of the monohydrazones of α-dicarbonyl compounds with Meldrum's acid gives the condensation products (13)—(19) under standard conditions. Reaction of pyruvaldehyde 2-phenylhydrazone or 2-t-butylhydrazone with Meldrum's acid at 80 °C gives the corresponding 2-substituted-2,3-dihydro-6-methyl-3-oxopyridazine-4-carboxylic acids (29) and (30). Cyclisation of the other *N*-monosubstituted condensation products (13), (14), (16), (18), and (19) to 3-oxopyridazine-4-carboxylic acids (31)—(35) can be effected under basic conditions. Gas-phase pyrolysis of the *N*-aryl derivatives (13)—(16) at 550 °C and 10^{-2} Torr gives *N*-arylpyridazin-3-ones (38)—(41) while the *N*-t-butyl derivatives (18) and (19) at 750 °C and 10^{-2} Torr give *N*-unsubstituted pyridazin-3-ones (44) and (45) by additional loss of 2-methylpropene. 2-t-Butylpyridazin-3-ones (42) and (43) can be isolated from the same precursors under milder conditions (500 °C and 10^{-2} Torr). Pyrolysis of the *N*,*N*-dimethyl derivative (17) gave only polymeric material.

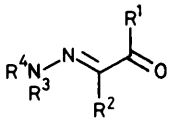
THIS paper describes a general and efficient two-step route to the pyridazin-3-one system (1). The six ring atoms of the heterocycle derive from Meldrum's acid [1] (2,2-dimethyl-1,3-dioxan-4,6-dione) (2) [C(3) and C(4)] and from α-dicarbonyl monohydrazones (azaenaminones) (3) [N(1), N(2), C(5), and C(6)]. The C(4)–C(5) bond is formed by Knoevenagel condensation of the two components, while cyclisation of the resulting products generates the lactam function of the pyridazinone (Scheme 1). The



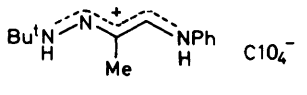
SCHEME 1

synthesis therefore represents an extension of the method of Schmidt and Druey [2,3] to allow the direct formation of 4-unsubstituted pyridazin-3-ones. Condensation of active methylene compounds with azaenaminones has also been reported by Severin,[4] while the formation of pyridin-2-ones from Meldrum's acid and certain enaminones has been studied.[5]

In order to assess properly the potential of the reaction, a range of hydrazones was employed, which includes the known *N*-aryl derivatives (4),[6] (5),[7] (6),[8] and (7) [9] and the *N*,*N*-dialkyl compound (8).[10] We have already commented on the scarcity of *N*-alkylhydrazones of α-dicarbonyl compounds,[11] and have therefore extended the series of t-butylhydrazones [11] to the pyruvaldehyde derivatives (10) and (11). The 2-t-butylhydrazone (10) could not be obtained from pyruvaldehyde dimethylacetal under the aqueous conditions employed for its *N*-phenyl analogue (6). Instead, reaction of the hydrazine with the acetal in methanolic solution gave the hydrazone (10) *without* the requirement of a separate hydrolysis step. The molecule of water needed may come from the initial condensation, or from potassium hydroxide used to neutralise the hydrazine hydrochloride.



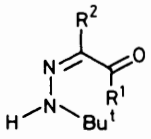
(4) $R^1 = R^2 = R^3 = H$, $R^4 = Ph$
(5) $R^1 = R^2 = R^3 = H$, $R^4 = p$-tolyl
(6) $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = Ph$
(7) $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Ph$
(8) $R^1 = R^2 = H$, $R^3 = R^4 = Me$
(9) $R^1 = R^2 = R^3 = H$, $R^4 = Bu^t$
(10) $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = Bu^t$
(11) $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Bu^t$



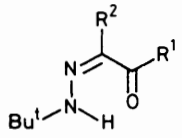
(12)

The 1-t-butylhydrazone (11) was obtained as the major product along with (10) by reaction of the hydrazine with pyruvaldehyde in water. The 1-hydrazone was readily obtained from the mixture by preferential reaction [12] of the 2-hydrazone with anilinium perchlorate to give the insoluble 1,2,5-triazapentadienium salt (12).

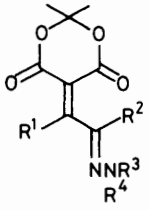
The observation of a significant allylic coupling $^4J_{2,NH}$ in the ^{1}H n.m.r. spectrum of (9) was interpreted as indicating a *Z*-s-*E* structure (A) for this compound.[11] A similar effect is also present in the spectrum of (11) (in [$^2H_6$]-DMSO), though in this case steric interaction between the t-butyl group and R^1 (= Me) makes structure



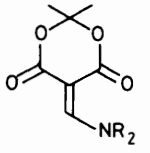
(A)



(B)



(13) $R^1 = R^2 = R^3 = H$, $R^4 = Ph$
(14) $R^1 = R^2 = R^3 = H$, $R^4 = p$-tolyl
(15) $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = Ph$
(16) $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Ph$
(17) $R^1 = R^2 = H$, $R^3 = R^4 = Me$
(18) $R^1 = R^2 = R^3 = H$, $R^4 = Bu^t$
(19) $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Bu^t$



(20)

(A) unlikely. Two isomers of (11) are present in deuteriochloroform solution. The major isomer [δ 7.0 (1 H, br s, NH), 6.95 (1 H, s), 2.28 (3 H, s), and 1.28 (s)] has almost certainly the same configuration as found in [$^2H_6$]-DMSO, while the minor isomer [δ 12.5 (1 H, br s, NH), 6.74 (1 H, s), 2.12 (3 H, s), and 1.28 (s)] is probably the hydrogen-bonded *Z*-s-*Z* structure (B) on account of the high-frequency position of the N*H* resonance. The co-existence of two isomers in solution is common in the enaminone series (*e.g.* ref. 11), but has not previously been observed with azaenaminones. The Table lists the ^{13}C n.m.r. parameters of the hydrazones (10) and (11), and, as expected,[11] the coupling constants are strongly dependent on the shape of the system. In particular, the large values of $^1J_{C-2,2-H}$, $^2J_{C-1,2-H}$, and $^3J_{C-2,NH}$ in the spectrum of the minor isomer of compound (11), relative to these of the major isomer, are typical of the *Z*-s-*Z* structure.[11]

Conditions for the Knoevenagel reaction of Meldrum's acid with aldehydes [13] and ketones [14,15] are well known. The 'aldehyde' condensation products (13)—(15), (17), and (18) were therefore synthesised in benzene solution at room temperature using piperidinium acetate as catalyst. The reaction time varied from a few minutes to 24 h. The *N*-arylhydrazones were most active, but this reactivity was surprisingly reduced by C-substitution (R^2 = Me), perhaps for steric reasons. The lower reactivity of the *N*-alkylhydrazones [especially (9)] is readily explained in terms of an increased electron density in the conjugated system which reduces the susceptibility of the carbonyl group to nucleophilic attack.

The 'ketone' condensation products (16) and (19) could both be obtained using pyridine as the solvent for the reaction,[14] though the yield of (19) was substantially increased by using titanium tetrachloride as catalyst.[15]

The n.m.r. spectra of the products (13)—(19) show similarities to those of the azaenaminone starting materials.[16] Thus, as expected on electronegativity grounds, the observed vicinal coupling ($R^1 = R^2 = H$) of 10—12 Hz is rather larger than in the azaenaminone series, but is in agreement with an s-*E* configuration. The small allylic coupling to N*H* (0.5—1.0 Hz) from R^2 = H in the t-butyl compounds (18) and (19) is also observed in azaenaminones (*cf.* above), and serves to assign the olefinic signals of (18). It is of interest that R^2 = H is the peak to highest frequency (δ 8.64) which represents a deshielding effect of more than 1.5 p.p.m. relative to the azaenaminone (9), though the chemical shifts of the corresponding carbon atoms are relatively similar [^{13}C n.m.r. δ (18) 132.27; δ (9) 133.06 [16]]. The large shift observed in the ^{1}H n.m.r. spectrum is therefore probably due to the proximity of the carbonyl group.

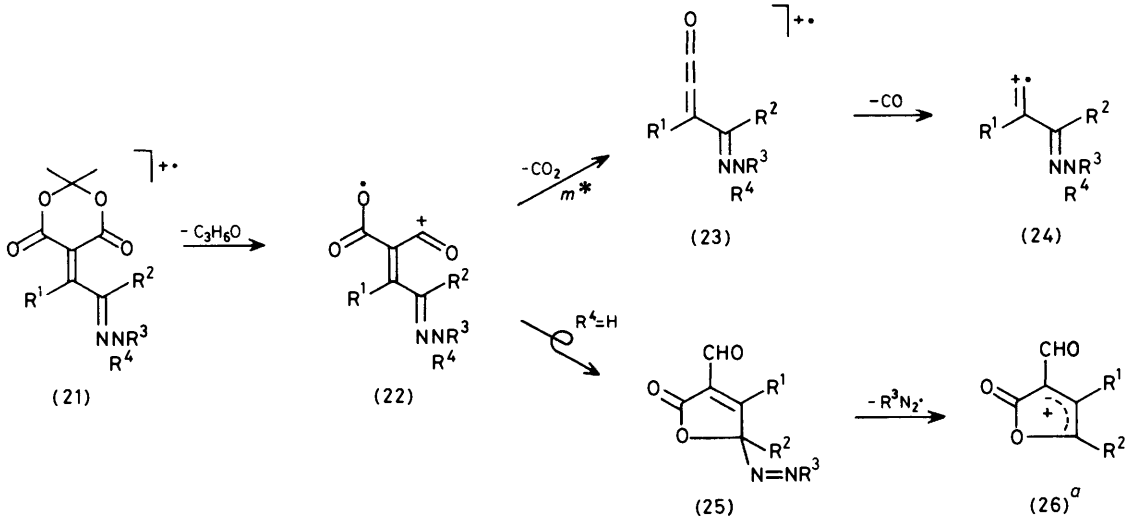
^{13}C N.m.r. spectra of pyruvaldehyde 1- and 2-t-butyl hydrazones [a]

Compd.	Isomer	δ(C*Me*$_3$)	δ(*C*Me$_3$)	δ(Me)	δ(C-1)	δ(C-2)	^1J	^2J	^3J
(10)		28.45	55.07	6.06	190.42	139.83	C(1)H(1) 176.5	C(2)H(1) 21.6	C(1)C*H*$_3$ 2.4
							2-*CH*$_3$ 127.8	C(2)C*H*$_3$ 6.1	*CH*$_3$H(1) 2.8
(11)	Major [b]	28.35	54.73	23.85	197.48	132.59	C(2)H(2) 163.5	C(1)H(2) 6.2	C(2)N*H* 2.7
							1-*CH*$_3$ 127.8	C(1)C*H*$_3$ 6.2	*CH*$_3$ H(2) 2.7
	Minor [b]	28.35	54.82	27.40	193.08	121.97	C(2)H(2) 182.6	C(1)H(2) 12.4	C(2)N*H* 5.3
	(*Z*-s-*Z*)						1-*CH*$_3$ 127.2	C(1)C*H*$_3$ 6.2	C(2)C*H*$_3$ 2.7

[a] Coupling constants quoted in Hz for solutions in deuteriochloroform. [b] Coupling constants measured at 90 MHz: assignments confirmed by deuterium exchange of N*H*.

Similar effects are observed in the *N*-aryl series (13)—(16), where assignments were confirmed by the effect of methyl substitution.

The *N*-methyl signal(s) of the *N,N*-dimethyl compound (17) show the effect of restricted rotation about the N–N bond. From the coalescence temperature (5 °C) and the separation of the two *N*-methyl singlets at −56 °C (32.5 Hz), the free energy of activation for this exchange process may be estimated as 58.0 kJ mol^{-1}. This is similar in magnitude to the corresponding bond rotation in (8) [16] ($\Delta G^{\ddagger}$ 51.2 kJ mol^{-1}), but is significantly smaller than that which has been recently reported for the related derivative (20; R = Me) [17] ($\Delta G^{\ddagger}$ 85.9 kJ mol^{-1}). In general, rotation around N–N bonds is more facile than around C–N bonds in (aza)enaminones and related systems.[16-18]

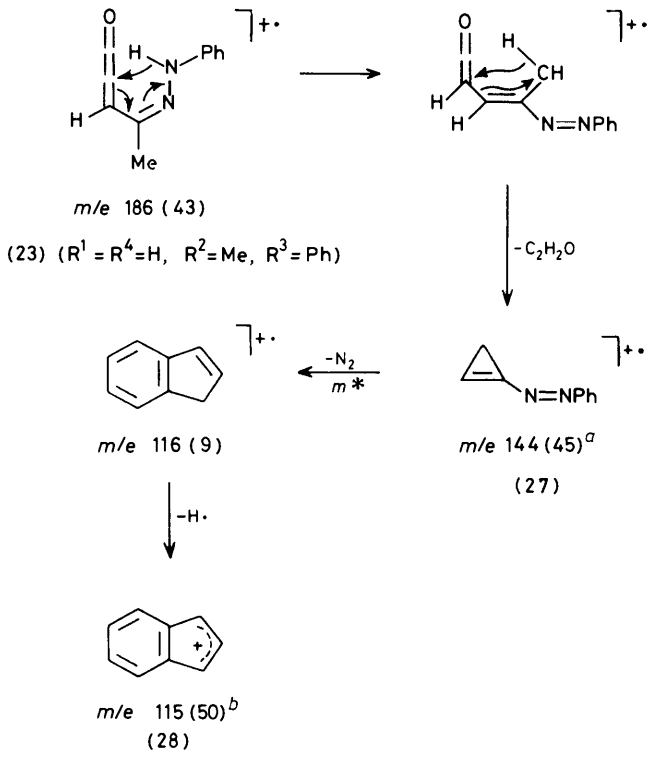


SCHEME 2 [a] From (13), Found: 111.0082. $C_5H_3O_3$ requires 111.0082. From (14), Found: 125.0237. $C_6H_5O_3$ requires 125.0239

The mass spectra of the condensation products (13)—(19) are of particular interest because of possible analogies with their thermal breakdown. In most cases, a significant mode of fragmentation from the molecular ion is the sequential loss of acetone, CO_2, and CO, as noted by Egger,[19] and this is the only major breakdown route for the *N,N*-dimethyl compound (17) (Scheme 2). However, for the *N*-monosubsubstituted compounds, hydrogen transfer and loss of the diazo-group can compete to give a fragment best represented as the lactone (26) (Scheme 2). This forms the base peak of the spectrum of compounds (16) and (19) (*i.e.* where R^1 = Me). For the *N*-t-butyl derivative (18) loss of the t-butyl group may precede the fragmentation of the ring, but the overall picture is similar to that of Scheme 2. In contrast, compound (15) (*i.e.* where R^2 = Me) shows an unexpected loss of the elements of keten from fragment (23) to give the cyclopropene radical cation (27) (or an isomer of this structure): loss of N_2 and a hydrogen atom gives the indenium cation (28) (Scheme 3).

The normal condensation product could not be obtained from Meldrum's acid and the azaenaminone (10). Under more vigorous conditions (80 °C, overnight), cyclisation occurred to give the 2,3-dihydro-3-oxopyridazine-4-carboxylic acid (29). Although this particular reaction produced a low and variable yield of product, the *N*-aryl analogue (30) was readily obtained from compound (6) after 2.5 h under reflux in benzene solution. In contrast, thermal cyclisation of the condensation products (13) and (16) (*i.e.* where R^2 = H could not be effected in solution even after extended reaction times (see Experimental section), possibly for steric reasons. However, the carboxylic acids (31)—(35) were obtained in typical yields of 60—80%, by the use of basic conditions (sodium methoxide in methanol) to catalyse the ring closure. Three factors may influence this reaction (Scheme 4). First, the acidity of the NH will govern the amount of the anion (36) which is present in solution. Second, the electron delocalisation in the anion will influence the various bond rotations necessary for the anion to adopt the reacting configuration. Both of these factors should be encouraged by the further delocalisation possible in the *N*-aryl series. The third possible factor, *viz.* the nucleophilicity of the attacking nitrogen atom, should be favoured in the *N*-alkyl series (provided steric effects are not of overriding importance). In practice, the reaction was particularly facile for the *N*-aryl derivatives, and so the rate-determining step is probably early in the reaction sequence. In an attempt to clarify this point, the t-butyl compound (18) was heated overnight in tetrahydrofuran in the presence of an *excess* of sodium hydride. That the starting material was recovered unchanged under these conditions suggests that isomerisation of the anion, which will be encouraged by a polar solvent (*e.g.* methanol) may be critical.

For reasons which are not apparent, the yield of the carboxylic acid (34) was much less than that of the other members of the series. In addition, a small quantity of a by-product was isolated, which was identified as the hydrazone (37) on the basis of its spectra. At 100 MHz, the ^{1}H n.m.r. spectrum shows virtual coupling in the

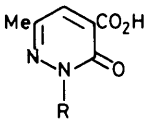


SCHEME 3 [a] Found: 144.0688. $C_9H_8N_2$ requires 144.0687. [b] Found: 115.0538. C_9H_7 requires 115.0548

complex signals due to the olefinic protons, but these could be analysed on a first-order basis at 360 MHz (see Experimental section). The hydrazone (37) probably arises by competitive nucleophilic attack of methoxide anion at C(4) of the dioxandione ring, as has been found for (20; R = H).[20]

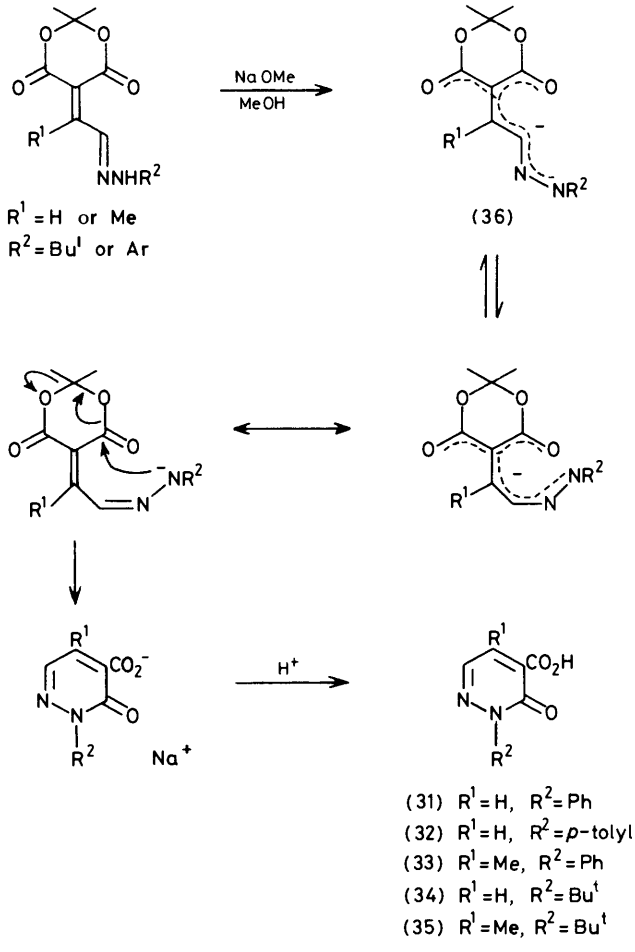
The carboxylic acids (29)—(35) were characterised by their spectra, and, in two cases, by decarboxylation to known pyridazin-3-ones (see below).

Following the work of Brown on the flash vacuum



(29) R = Bu^t
(30) R = Ph

pyrolysis of Meldrum's acid derivatives,[21] we have employed this technique as a means of generating the unsaturated lactam function.[22] Gas-phase pyrolysis of the condensation products (13)—(16) leads directly to the pyridazin-3-ones (38)—(41), in isolated yields of up to 83%. However, pyrolysis of the t-butyl derivatives (18) and (19) under the mildest conditions for complete disappearance of the starting material (500 °C and 10^{-2} Torr) each gave two pyridazin-3-one products. These were identified as the *N*-t-butyl compounds (42) and (43) respectively and the *N*-unsubstituted compounds (44) and (45) respectively. The latter compounds are probably formed by concerted loss of 2-methylpropene from the *N*-t-butyl derivatives, and they can be obtained exclusively by pyrolysis at a higher furnace temperature (750 °C). The ratio of the *N*-t-butyl and *N*-unsubstituted products varies in a regular manner at intermediate temperatures (Figure), but the overall temperature profile is rather flat. Similar loss of t-butyl substituents has been observed in pyrolyses of t-butyl esters:[23] in all these examples, the t-butyl group acts as the synthetic equivalent of a hydrogen atom.

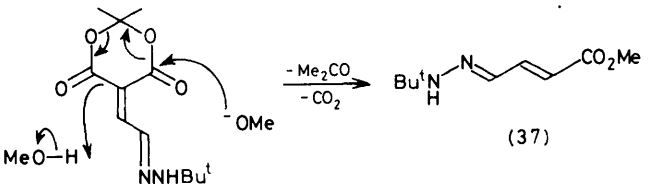


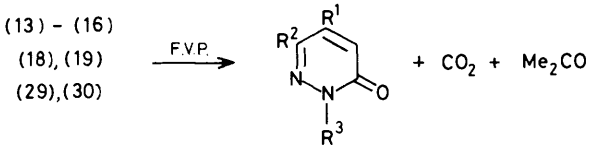
SCHEME 4

The *N*-t-butylpyridazin-3-ones (42) and (43) are mobile liquids which can be distilled without decomposition. On a preparative scale, this volatility allows facile separation from the corresponding *N*-unsubstituted compound (see Experimental section).

Flash vacuum pyrolysis of the *N*,*N*-dimethyl compound (17) at 600 °C gave only polymeric material, probably due to intermolecular reactions of an intermediate methyleneketen.

Decarboxylation of the carboxylic acids (29) and (30) was also conveniently effected by flash vacuum pyrolysis, and proved the method of choice for the preparation of the 6-methyl-2-phenyl derivative (40). The *N*-t-butyl and *N*-unsubstituted pyridazin-3-ones (46) and (47) were obtained from (29) under similar reaction condi-





(38) $R^1 = R^2 = H$, $R^3 = Ph$
(39) $R^1 = R^2 = H$, $R^3 = p$-tolyl
(40) $R^1 = H$, $R^2 = Me$, $R^3 = Ph$
(41) $R^1 = Me$, $R^2 = H$, $R^3 = Ph$
(42) $R^1 = R^2 = H$, $R^3 = Bu^t$
(43) $R^1 = Me$, $R^2 = H$, $R^3 = Bu^t$
(44) $R^1 = R^2 = R^3 = H$,
(45) $R^1 = Me$, $R^2 = R^3 = H$
(46) $R^1 = H$, $R^2 = Me$ $R^3 = Bu^t$
(47) $R^1 = R^3 = H$, $R^2 = Me$

tions to those described for the condensation products (18) and (19).

Most of the pyridazin-3-ones (38)—(47) are known compounds, and were characterised by their melting points and by their spectra. In the ^1H n.m.r. spectra,[24]

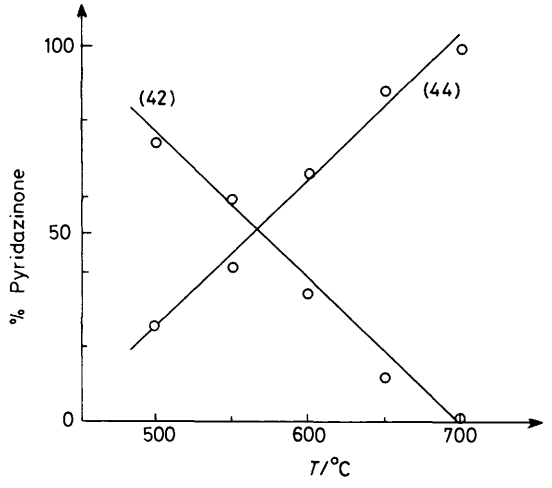
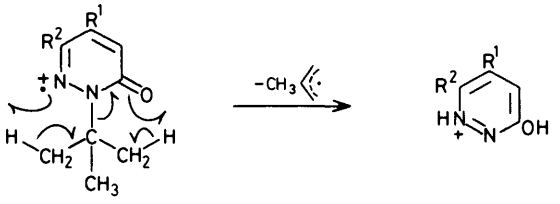


FIGURE Temperature dependence of products from the pyrolysis of compound (18)

coupling constants are observed as follows: $^3J_{45}$ *ca.* 9, $^3J_{56}$ *ca.* 3.5, $^4J_{46}$ *ca.* 2, and $^4J_{5\text{-}CH_3,4}$ *ca.* 1 Hz. No long-range coupling to 6-methyl groups was resolved. In the mass spectra of the *N*-aryl and *N*-unsubstituted [25,26] compounds, the molecular ion is the base peak of the spectrum. Loss of CO or CHO from the molecular ion is followed either by cleavage of the N(1)–N(2) fragment or of the N(1)–C(6) fragment. The spectra of the *N*-t-butyl compounds (42), (43), and (46) are anomalous, since the base peak is formed by loss of a 2-methylallyl *radical* from the molecular ion to give a pyridazinium cation, *e.g.* (48) (Scheme 5). Similarly, the *N*-t-butyl carboxylic



$R^1 = R^2 = H$: *m/e* 152 (18) *m/e* 97 (100)[a]
$R^1 = Me$, $R^2 = H$: *m/e* 166 (20) *m/e* 111 (100)
$R^1 = H$, $R^2 = Me$: *m/e* 166 (27) *m/e* 111 (100)

(48)

SCHEME 5 [a] Found: 97.0424. $C_4H_5N_2O$ requires 97.0402

acids (29), (34), and (35) lose C_4H_7 followed by H_2O, rather than the cleavage of CO_2 found for the *N*-aryl examples.

In conclusion, the work presented in this paper represents a general method for the preparation of 2-, 5-, and 6-substituted pyridazin-3-ones, and the corresponding 4-carboxylic acids, in three steps, from commercially available starting materials, In general, the yields are good, the synthetic intermediates are readily made, and there are few problems in work-up. The method seems to be particularly applicable to 5-substituted pyridazin-3-ones, which have hitherto been most often prepared as (separable) components of a mixture of pyridazin-3-one isomers,[27,28] or by means which are not capable of generalisation.[29] The chief disadvantage of the Meldrum's acid route is probably the availability of the azaenaminone precursors, especially in the *N*-alkyl series. However, good methods now exist for specific *N*-alkylation of *N*-unsubstituted pyridazin-3-ones [30] (available *via* the *N*-t-butyl compounds) and these significantly generalise the range of compounds accessible by the present method.

EXPERIMENTAL

^1H and ^{13}C N.m.r. spectra were recorded at 100 and 20 MHz respectively, unless otherwise stated.

Pyruvaldehyde 2-t-Butylhydrazone (10).—A solution of t-butylhydrazine [from t-butylhydrazine hydrochloride (6.2 g, 50 mmol) and potassium hydroxide (2.8 g, 50 mmol)] in methanol (50 ml) was added to a solution of pyruvaldehyde dimethyl acetal (5.9 g, 50 mmol) in methanol (20 ml) and the resulting suspension was set aside at room temperature overnight. Ether (50 ml) was added to the mixture and the precipitated potassium chloride was filtered off. The filtrate was concentrated to leave a semi-solid material which was recrystallised (with hot filtration) from cyclohexane. Final purification by bulb-to-bulb distillation gave the *hydrazone* (3.45 g, 49%) as a colourless solid, m.p. 63—65 °C (from cyclohexane), ^1H n.m.r. δ ($CDCl_3$) 9.26 (1 H, s),

ca. 6.1 (1 H, br s), 1.76 (3 H, s), and 1.32 (9 H, s); *m/e* 142 (M^+, 21%), 127 (9), 85 (25), 72 (9), 58 (38), 57 (100), 42 (30), and 41 (27) (Found: C, 58.9; H, 10.05; N, 19.55. $C_7H_{14}N_2O$ requires C, 59.15; H, 9.85; N, 19.7%).

Pyruvaldehyde 1-*t-Butylhydrazone* (11).—A solution of t-butylhydrazine [from t-butylhydrazine hydrochloride (6.21 g, 50 mmol) and potassium hydroxide (2.8 g, 50 mmol)] in water (20 ml) was added slowly to a solution of pyruvaldehyde (40%, 6 ml) in water (30 ml), and the mixture was set aside for 30 min. The oil which formed was extracted with methylene dichloride (3 × 50 ml) and the organic extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* to give an orange oil (6.25 g) which was shown by ^{1}H n.m.r. spectroscopy to be a 2 : 1 mixture of the 1- and 2-t-butylhydrazones respectively. The oil was then added to a solution of anilinium perchlorate (3.0 g, 15.5 mmol) in ethanol (5 ml). After 2 min, ether was added, and the precipitate of 1-*t-butyl*-3-*methyl*-5-*phenyl*-1H-1,2,5-*triazapentadienium perchlorate* (12) (2.61 g) was filtered off. The filtrate was concentrated and flash distilled at 140 °C and 16 Torr to give the pure 1-*hydrazone* (2.55 g, 36%), b.p. 120—122 °C (16 Torr), ^{1}H n.m.r. δ ([$^2H_6$]-DMSO) 8.88 (1 H, s, NH), 7.00 (1 H, d, ^4J 2.0 Hz, assignment of coupling confirmed by deuterium exchange), 2.15 (3 H, s), and 1.21 (9 H, s); *m/e* 142 (M^+, 30%), 85 (72), 57 (100), 43 (54), and 41 (36) (Found: C, 59.3; H, 10.15; N, 19.55. $C_7H_{14}N_2O$ requires C, 59.15; H, 9.85; N, 19.7%).

The *triazapentadienium salt* (12) obtained as a by-product of the work-up had m.p. 185—186 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ([$^2H_6$]acetone) 8.73 (1 H, s), 7.4—7.8 (5 H, complex), 2.27 (3 H, s), and 1.46 (9 H, s) (Found: C, 49.3; H, 6.45; N, 13.05. $C_{13}H_{20}ClN_3O_4$ requires C, 49.15; H, 6.3; N, 13.25%).

General Methods for the Preparation of 5-(1,2-*Diazabutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione Derivatives*. —*Method A*.[13] A suspension of 2,2-dimethyl-1,3-dioxan-4,6-dione (1.44 g, 10 mmol) and the α-dicarbonyl monohydrazone (10 mmol) in benzene (15 ml) was treated with acetic acid (5 drops) and with piperidine (5 drops); the mixture was then stirred at room temperature. The precipitated condensation product was filtered off and thoroughly washed with light petroleum.

Method B.[14] A suspension of 2,2-dimethyl-1,3-dioxan-4,6-dione (1.44 g, 10 mmol) and the α-dicarbonyl monohydrazone (10 mmol) in pyridine (5 ml) was stirred at room temperature for 24 h. The solution was concentrated and the product was filtered off and washed with ether.

Method C.[15] A solution of titanium tetrachloride (2.2 ml, 20 mmol) in carbon tetrachloride (5 ml) was added dropwise to ice-cold tetrahydrofuran (40 ml). This was followed by slow addition of a solution of 2,2-dimethyl-1,3-dioxan-4,6-dione (1.44 g, 10 mmol) and the α-dicarbonyl monohydrazone (10 mmol) in tetrahydrofuran (10 ml), and then by a solution of pyridine (3.2 ml) in tetrahydrofuran (5 ml). The stirring was continued for 1 h at 0 °C, and at room temperature overnight, after which water (10 ml) and ether (20 ml) were added. The organic layer was separated, washed with brine and with saturated aqueous sodium hydrogen carbonate, and then dried and concentrated. The product was washed with a small amount of light petroleum.

The following products were made by these methods: 5-(1,2-*diaza*-1-*phenylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (13) (Method A, stirred for 30 min) (2.53 g, 93%), m.p. 200—203 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) 8.95 (1 H, d, ^3J 11.5 Hz), 8.32 (1 H, d, ^3J 11.5 Hz), 7.3—7.4 (5 H, complex), and 1.76 (6 H, s); *m/e* 274 (M^+, 38%), 216 (56), 172 (54), 144 (20), 111 (60), 93 (20), 92 (28), 77 (100), 65 (40), 51 (18), and 43 (54) (Found: C, 61.5; H, 5.05; N, 10.25. $C_{14}H_{14}N_2O_4$ requires C, 61.3; H, 5.1; N, 10.2%): 5-(1,2-*diaza*-1-p-*tolylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (14) (Method A, stirred for 30 min) (2.90 g, quantitative), m.p. 188—189 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ([$^2H_6$]-DMSO) 8.62 (1 H, d, ^3J 11.5 Hz), 7.88 (1 H, d, ^3J 11.5 Hz), 7.18 (4 H, s), 2.26 (3 H, s), and 1.64 (6 H, s); *m/e* 288 (M^+, 47%), 230 (67), 186 (55), 158 (27), 111 (33), 106 (44), 91 (100), 79 (20), 77 (29), 65 (20), and 43 (31) (Found: C, 62.3; H, 5.55; N, 9.6. $C_{15}H_{16}N_2O_4$ requires C, 62.5; H, 5.55; N, 9.7%): 5-(1,2-*diaza*-3-*methyl*-1-*phenylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (15) (Method A, stirred overnight) (2.35 g, 82%), m.p. 139—140 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ([$^2H_6$]-acetone) 8.04 (1 H, s), 7.2—7.6 (5 H, complex), 2.26 (3 H, s), and 1.75 (6 H, s); *m/e* 288 (M^+, 1%), 230 (90), 186 (43), 144 (45), 115 (50), 77 (86), and 43 (100) (Found: C, 62.25; H, 5.55; N, 9.6. $C_{15}H_{16}N_2O_4$ requires C, 62.5; H, 5.55; N, 9.7%): 5-(1,2-*diaza*-4-*methyl*-1-*phenylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (16) (Method B), (1.48 g, 52%), m.p. 171—172 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ([$^2H_6$]-DMSO) 8.88 (1 H, s), 7.2—7.5 (5 H, complex), 2.65 (3 H, s), and 1.67 (6 H, s); *m/e* 288 (M^+, 43%), 230 (58), 212 (25), 186 (71), 185 (43), 158 (23), 157 (15), 125 (100), 93 (29), 92 (42), 77 (83), 65 (38), 53 (40), and 43 (71) (Found: C, 62.4; H, 5.4; N, 9.8. $C_{15}H_{16}N_2O_4$ requires C, 62.5; H, 5.55; N, 9.7%), 5-(1,2-*diaza*-1,1-*dimethylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (17) (Method A, stirred for 90 min, solvent evaporated, (2.14 g, 95%), m.p. 119—121 °C (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) 8.17 (1 H, d, ^3J 10.0 Hz), 8.03 (1 H, d, ^3J 10.0 Hz), 3.38 (6 H, br s), and 1.72 (6 H, s); *m/e* 226 (M^+, 46%), 168 (100), 125 (17), 124 (24), 109 (13), 95 (7), 69 (89), 58 (93), and 43 (100); ^{13}C n.m.r. δ ($CDCl_3$) 163.51 (q), 161.66 (q), 155.66, 127.52, 103.57 (q), 102.43 (q), *ca.* 44 (br), and 27.04 (Found: C, 53.3; H, 6.3; N, 12.35. $C_{10}H_{14}N_2O_4$ requires C, 53.1; H, 6.25; N, 12.4%): 5-(1,2-*diaza*-1-*t-butylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (18). (Method A, stirred overnight) (1.95 g, 77%), m.p. 194 °C (decomp.) (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) 8.64 (1 H, d, ^3J 10.5 Hz), 8.20 (1 H, d, ^3J 10.5 Hz), 1.70 (6 H, s), and 1.37 (9 H, s); *m/e* 254 (M^+, 20%), 196 (12), 141 (42), 139 (50), 111 (88), and 57 (100); ^{13}C n.m.r. δ ($CDCl_3$) 163.76 (q), 163.23 (q), 156.54, 132.27, 103.76 (q), 99.75 (q), 57.71 (q), 28.06, and 27.04 (Found: C, 56.8; H, 7.15; N, 11.0. $C_{12}H_{18}N_2O_4$ requires C, 56.7; H, 7.15; N, 11.0%): 5-(1,2-*diaza*-1-*t-butyl*-4-*methylbutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione* (19) (Method C) (1.88 g, 70%), m.p. 165—167 °C (decomp.) (from cyclohexane), ^{1}H n.m.r. ($CDCl_3$) 8.76 (1 H, d, ^4J 1.0 Hz, assignment of coupling confirmed by deuterium exchange), 8.38 (1 H, br s, N*H*), 2.68 (3 H, s), 1.68 (6 H, s), and 1.31 (9 H, s); *m/e* 268 (M^+, 9%), 210 (6), 125 (100), 67 (9), 57 (48), 43 (11), and 41 (15); ^{13}C n.m.r. δ ($CDCl_3$) 168.73 (q), 163.04 (q), 162.50 (q), 133.01, 104.88 (q), 102.14 (q), 56.53 (q), 28.43, 26.70, and 17.45 (Found: C, 58.1; H, 7.25; N, 10.4. $C_{13}H_{20}N_2O_4$ requires C, 58.2; H, 7.45; N, 10.45%). Method B gave this product in 6.9% yield.

2-*t-Butyl*-2,3-*dihydro*-6-*methyl*-3-*oxopyridazine*-4-*carboxylic Acid* (29).—A solution of 2,2-dimethyl-1,3-dioxan-4,6-dione (1.44 g, 10 mmol) and pyruvaldehyde 2-t-butylhydrazone (1.42 g, 10 mmol) was heated under reflux for 40 h in benzene (25 ml) containing acetic acid (10 drops) and piperidine (10 drops). The dark solution was extracted

with aqueous sodium hydroxide (1M; 3 × 20 ml) and the combined aqueous layers were washed with ether (20 ml), and then acidified with dilute hydrochloric acid. The solution was extracted with methylene dichloride (4 × 20 ml), and the combined organic extracts were dried (Na_2SO_4) and concentrated. The *acid* (0.42 g, 20%), which crystallised on treatment of the residue with a small amount of propan-2-ol in hexane at −30 °C, had m.p. 86—88 °C (from hexane), ^{1}H n.m.r. δ ($CDCl_3$) 8.06 (1 H, s), 2.46 (3 H, s), and 1.69 (9 H, s); *m/e* 210 (M^+, 21%), 192 (10), 166 (19), 155 (100), 137 (43), 111 (49), 110 (79), 108 (28), 80 (28), 57 (94), 44 (30), and 41 (62); ^{13}C n.m.r. δ ($CDCl_3$) 163.08 (q), 162.12 (q), 144.57 (q), 134.90, 125.22 (q). 67.02 (q), 27.00, and 20.23 (Found: C, 57.3; H, 6.95; N, 13.35. $C_{10}H_{14}N_2O_3$ requires C, 57.15; H, 6.65; N, 13.35%).

2,3-Dihydro-6-methyl-2-phenyl-3-oxopyridazine-4-carboxylic Acid (30).—A solution of 2,2-dimethyl-1,3-dioxan-4,6-dione (1.44 g, 10 mmol) and pyruvaldehyde 2-phenylhydrazone (1.62 g, 10 mmol) in benzene (50 ml) containing acetic acid (10 drops) and piperidine (10 drops) was heated under reflux for 2.5 h. The cooled solution was extracted with aqueous sodium hydroxide (1M; 3 × 25 ml). The combined aqueous extracts were acidified (HCl) and extracted with methylene dichloride (3 × 50 ml). The organic extracts were dried (Na_2SO_4) and concentrated to give a red oil which crystallised on trituration with ethanol. The *acid* (1.29 g, 56%) so obtained had m.p. 102—103 °C (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) *ca.* 13.5 (br s), 8.15 (1 H, s), 7.4—7.6 (5 H, complex), and 2.51 (3 H, s); *m/e* 230 (M^+, 93%), 186 (45), 157 (10), 117 (15), 91 (15), 77 (100), and 51 (35); ^{13}C n.m.r. δ ($CDCl_3$) 162.83 (q), 161.44 (q), 147.33 (q), 139.94 (q), 136.60, 129.21, 128.89, 126.33 (q), 125.14, and 20.81 (Found: C, 62.4; H, 4.4; N, 12.1. $C_{12}H_{10}N_2O_3$ requires C, 62.6; H, 4.3; N, 12.15%).

Reaction of Glyoxal Monophenylhydrazone with 2,2-Dimethyl-1,3-dioxan-4,6-dione in Hot Benzene.—A solution of the hydrazone (1.48 g, 10 mmol) and the dione (1.44 g, 10 mmol) in benzene (50 ml) containing acetic acid (10 drops) and piperidine (10 drops) was heated under reflux for 6 h. The resulting dark solution was extracted with aqueous sodium hydroxide (3 × 20 ml), and the basic extracts were acidified. The brown solid (1.28 g) which was precipitated was identified by ^{1}H n.m.r. spectroscopy as the condensation product (13) (46% recovery). There was no evidence for cyclisation under these conditions.

Attempted Thermolysis of 5-(1,2-Diaza-4-methyl-1-phenylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (16) *in Benzene.*—A suspension of the butadienylidenedioxandione (16) (0.57 g, 2 mmol) in benzene (10 ml) was heated under reflux for 6.5 h. The solvent was removed under reduced pressure to give a red solid (0.51 g) the ^{1}H n.m.r. spectrum of which was identical with that of the starting material. The recovery was 90%.

Preparation of 2,3-Dihydro-3-oxopyridazine-4-carboxylic Acids by Cyclisation of 5-(1,2-Diazabutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-diones under Basic Conditions.—A solution of the butadienylidenedioxandione (2 mmol) in methanolic sodium methoxide [from sodium (0.05 g, slight excess) and methanol (10 ml)] was heated under reflux for the length of time stated. If necessary, ether was added to the cooled mixture to complete the precipitation of the sodium salt of the carboxylic acid. This salt was filtered off, dissolved in water (10 ml), and the solution acidified with dilute hydrochloric acid (1M; 5 ml). The resulting carboxylic acid was extracted into methylene dichloride (2 × 25 ml) and the combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the *acid* as a crystalline solid.

The following pyridazines were made in this way: *2,3-dihydro-2-phenyl-3-oxopyridazine-4-carboxylic acid* (31) (20 min reflux) (0.28 g, 65%), m.p. 95—96 °C (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) 14.6 (br, OH), 8.26 (2 H, s), and 7.4—7.6 (5 H, complex); *m/e* 216 (M^+, 100%), 172 (35), 77 (74), 51 (23), and 39 (19); ^{13}C n.m.r. δ ($CDCl_3$) 162.54 (q), 162.33 (q), 139.86 (q), 138.31, 134.75, 129.47, 128.94, 126.87 (q), and 125.07 (Found: C, 61.15; H, 3.75; N, 12.7. $C_{11}H_8N_2O_3$ requires C, 61.1; H, 3.7; N, 12.95%): *2,3-dihydro-2-p-tolyl-3-oxopyridazine-4-carboxylic acid* (32) (20 min reflux) (0.29 g, 63%), m.p. 200—201 °C (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$/[$^2H_6$]-DMSO) 8.29 (1 H, d, ^3J 3.9 Hz), 8.20 (1 H, d, ^3J 3.9 Hz), 7.44 (2 H, d), 7.30 (2 H, d), and 2.41 (3 H, s) (OH not apparent, δ 0—15); *m/e* 230 (M^+, 100%), 186 (31), 91 (62), 65 (19), and 39 (19); ^{13}C n.m.r. ($CDCl_3$) 162.69 (q), 162.44 (q), 139.89 (q), 138.17, 137.46 (q), 134.60, 129.59, 126.86 (q), 124.85, and 21.10 (Found: C, 62.4; H, 4.35; N, 12.05. $C_{12}H_{10}N_2O_3$ requires C, 62.6; H, 4.35; N, 12.15%): *2,3-dihydro-5-methyl-2-phenyl-3-oxopyridazine-4-carboxylic acid* (33) (20 min reflux) (0.36 g, 78%), m.p. 111—114 °C (from ethanol), ^{1}H n.m.r. δ ($CDCl_3$) 14.4 (v br, OH), 8.04 (1 H, s), 8.4—8.6 (5 H, complex), and 2.78 (3 H, s); *m/e* 230 (M^+, 100%), 212 (30), 186 (36), 91 (10), 77 (55), 55 (14), 51 (23), and 39 (14); ^{13}C n.m.r. ($CDCl_3$) 163.60 (q), 162.39 (q), 150.50 (q), 142.76, 140.01 (q), 129.28, 128.93, 125.12, 122.84 (q), and 19.61 (Found: C, 62.4; H, 4.55; N, 11.8. $C_{12}H_{10}N_2O_3$ requires C, 62.6; H, 4.35; N, 12.15%): *2-t-butyl-2,3-dihydro-5-methyl-3-oxopyridazine-4-carboxylic acid* (35) (reflux overnight, solvent concentrated before addition of ether) (0.32 g, 76%), m.p. 123—125 °C (from hexane), ^{1}H n.m.r. δ ($CDCl_3$), 7.88 (1 H, s), 2.70 (3 H, s), and 1.68 (9 H, s) (OH not apparent, δ 0—15); *m/e* 210 (M^+, 20%), 192 (17), 166 (13), 155 (100), 137 (73), 111 (40), 110 (50), 98 (23), 57 (73), 41 (40), and 39 (23); ^{13}C n.m.r. δ ($CDCl_3$) 164.47 (q), 163.50 (q), 148.94 (q), 140.53, 122.36 (q), 67.82 (q), 27.54, and 19.20 (Found: C, 56.95; H, 6.8; N, 13.15. $C_{10}H_{14}N_2O_3$ requires C, 57.15; H, 6.65; N, 13.35%).

The preparation of 2-t-butyl-2,3-dihydro-3-oxopyridazine-4-carboxylic acid (34) required a slightly modified procedure. Thus, freshly recrystallised 5-(1,2-diaza-1-t-butylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (18) (0.51 g, 2 mmol) was heated under reflux overnight in methanol (10 ml) containing sodium methoxide [from sodium (0.05 g, slight excess)]. The solvent was evaporated under reduced pressure and the residue was dissolved in water (10 ml); the solution was filtered free from a small quantity of undissolved solid (see below) and then acidified with dilute hydrochloric acid (1M; 5 ml). The mixture was extracted with methylene dichloride (3 × 20 ml) and the combined organic extracts were dried (Na_2SO_4) and concentrated to leave a brown gum. This residue was boiled with hexane (15 ml), which was decanted and cooled to −30 °C, whereupon the *acid* (0.10 g, 26%) crystallised. It had m.p. 62—64 °C (from hexane), ^{1}H n.m.r. δ ($CDCl_3$) 14.2 (v br, OH), 8.15 (1 H, d, ^3J 3.9 Hz), 8.08 (1 H, d, ^3J 3.9 Hz), and 1.70 (9 H, s); *m/e* 196 (M^+, 11%), 178 (10), 152 (8), 141 (95), 123 (34), 97 (20), 96 (31), 84 (17), 57 (100), 41 (44), and 39 (22); ^{13}C n.m.r. δ ($CDCl_3$) 163.73 (q), 163.59 (q), 136.15, 133.76, 126.15 (q), 68.43 (q), and 27.53 (Found: C, 55.3; H, 6.25; N, 14.0. $C_9H_{12}N_2O_3$ requires C, 55.1; H, 6.1; N, 14.3%).

The solid (0.04 g) which was filtered off (see above) was dissolved in 50% hexane–ether, and the solution was passed

down an alumina column (5 × 0.5 cm). It was identified from its spectra as the t-butylhydrazone of methyl 4-formylbut-2-enoate (37) (1%), m.p. 91—93 °C (from hexane), ^{1}H n.m.r. (first order at 360 MHz), δ ($CDCl_3$) 7.38 (1 H, dd, ^3J 9.7, ^3J 15.4 Hz), 7.25 (1 H, d, ^3J 9.7 Hz), 5.81 (1 H, d, ^3J 15.4 Hz), 3.73 (3 H, s), and 1.21 (9 H, s); *m/e* 184 (M^+, 31%), 169 (86), 153 (10), 112 (29), 97 (31), 80 (16), 69 (41), 57 (100), 42 (24), 41 (48), and 39 (24) (Found: C, 58.5; H, 8·85; N, 15.0. $C_9H_{16}N_2O_2$ requires C, 58.7; H, 8.7; N; 15.2%).

In an attempt to avoid this side-reaction, the cyclisation of (18) was attempted using an excess of sodium hydride in tetrahydrofuran. After the mixture had been heated under reflux overnight, the hydride was destroyed with methanol and the solution was acidified to give unchanged starting material (89%) upon standard work-up.

Gas-phase Pyrolyses.—The apparatus and general technique have been described previously.[7] Small-scale pilot experiments (0.1—0.3 mmol) were employed to optimise furnace and inlet conditions, and to monitor the temperature-dependence of the t-butyl compound thermolyses. For these experiments, the entire pyrolysate was dissolved in deuteriochloroform (0.3—0.5 ml) and analysed by ^{1}H n.m.r. spectroscopy. For the preparative pyrolyses, the yields quoted are of isolated material, pure by ^{1}H and ^{13}C n.m.r.

2-Arylpyridazin-3(2H)-*ones.*—The appropriate 5-(diazabutadienylidene)dioxandione (5 mmol) was sublimed or distilled at 10^{-2}—10^{-3} Torr through a silica tube (30 × 2.5 cm) held at 550 °C. The pyrolysate consisted of three fractions. First, a small quantity of dark polymeric material at the exit point of the furnace was removed with a tissue soaked in methylene dichloride. The most volatile fraction, which had been trapped in liquid nitrogen, was removed with a dropper, and this portion of the trap was rinsed with methylene dichloride. The major fraction, which in most cases had crystallised, was then dissolved in methylene dichloride, which was subsequently removed under reduced pressure to give the pyridazinone.

The following 2-arylpyridazinones were made by this method: 2-phenylpyridazin-3(2*H*)-one (38) (0.49 g, 57%), m.p. 107—108 °C (from cyclohexane) (lit.,[31] 107—109 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.85 (1 H, dd, $^3J_{65}$ 3.5, $^4J_{64}$ 1.8 Hz), 7.3—7.7 (5 H, complex), 7.20 (1 H, dd, $^3J_{56}$ 3.5, $^3J_{54}$ 9.4 Hz), and 7.01 (1 H, dd, $^3J_{45}$ 9.4, $^4J_{46}$ 1.8 Hz); *m/e* 172 (M^+, 100%), 171 (48), 144 (26), 77 (48), 51 (19), and 39 (43); [(from 5-(1,2-diaza-1-phenylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (13), inlet temperature 190—200 °C, pyrolysis time 3 h, inlet residue 18%]: 2-*p*-tolylpyridazin-3(2*H*)-one (39) (0.55 g, 59%), m.p. 97—99 °C (from cyclohexane) (lit.,[32] 101—103 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.83 (1 H, dd, $^3J_{65}$ 3.5, $^4J_{64}$ 1.8 Hz), 7.45 (2 H, d), 7.24 (2 H, d), 7.19 (1 H, dd, $^3J_{56}$ 3.5, $^3J_{54}$ 9.4 Hz), 6.98 (1 H, dd, $^3J_{45}$ 9.4, $^4J_{46}$ 1.8 Hz), and 2.37 (3 H, s); *m/e* 186 (M^+, 100%), 185 (35), 158 (26), 106 (13), 105 (12), 91 (55), 65 (23), and 39 (52); [from 5-(1,2-diaza-1-*p*-tolylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (14), inlet temperature 190—200 °C, pyrolysis time 3 h, inlet residue 20%]: 6-methyl-2-phenylpyridazin-3(2*H*)-one (40) (0.35 g, 38%), m.p. 77—78 °C (from cyclohexane) (lit.,[33] 79—80 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.3—7.7 (5 H, complex), 7.10 (1 H, d, $^3J_{54}$ 9.2 Hz), 6.92 (1 H, d, $^3J_{45}$ 9.2 Hz), and 2.33 (3 H, s); *m/e* 186 (M^+, 100%), 185 (42), 158 (15), 157 (14), 144 (12), 115 (14), 77 (48), 53 (26), and 51 (16) [from 5-(1,2-diaza-3-methyl-1-phenylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (15), inlet temperature 130—140 °C, pyrolysis time 1 h, inlet residue 20%; this pyridazinone is made more cleanly from the 4-carboxylic acid (20) (see below)]: 5-methyl-2-phenylpyridazin-3(2*H*)-one (41) (0.77 g, 83%), m.p. 84—84.5 °C (from cyclohexane) (lit.,[29] 84 °C) ^{1}H n.m.r. δ ($CDCl_3$) 7.69 (1 H, d, $^4J_{64}$ 2.0 Hz), 7.3—7.6 (5 H, complex), 6.78 (1 H, overlapping dq, $^4J_{46}$ 2.0, $^4J_{4,CH_3}$ 1.3 Hz), and 2.21 (3 H, d, $^4J_{CH_3,4}$ 1.3 Hz); *m/e* 186 (M^+, 100%), 185 (41), 158 (13), 157 (12), 77 (34), 53 (31), 39 (10) [from 5-(1,2-diaza-4-methyl-1-phenylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (16), inlet temperature 180 °C, pyrolysis time 1 h, inlet residue 6%].

Pyridazin-3(2H)-*ones.*—The appropriate 5-(diaza-1-t-butylpentadienylidene)dioxandione (2 mmol) was pyrolysed at 750 °C and 10^{-2}—10^{-3} Torr. Work-up conditions were similar to those described for the 2-aryl derivative.

The following pyridazinones were made by this method: pyridazin-3(2*H*)-one (44) (0.12 g, 63%), m.p. 103 °C (after sublimation) (lit.,[34] 103—104 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.82 (1 H, dd, $^3J_{65}$ 3.6, $^4J_{64}$ 1.6 Hz), 7.25 (1 H, dd, $^3J_{56}$ 3.6, $^3J_{54}$ 9.5 Hz), and 6.99 (1 H, dd, $^3J_{45}$ 9.5, $^4J_{46}$ 1.6 Hz); *m/e* 96 (M^+, 100%), 68 (33), 42 (13), 41 (13), and 39 (40) [from 5-(1,2-diaza-1-t-butylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (18), inlet temperature 160 °C, pyrolysis time 1.5 h, inlet residue 6%]: 5-methylpyridazin-3(2*H*)-one (45) (0.16 g, 73%), m.p. 151—153 °C (from cyclohexane) (lit.,[27] 151—153 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.65 (1 H, d, $^4J_{64}$ 1.8 Hz), 6.72 (1 H, overlapping dq, $^4J_{46}$ 1.8, $^4J_{4,CH_3}$ 1.3 Hz), and 2.21 (3 H, d, $^4J_{CH_3,4}$ 1.3 Hz); *m/e* 110 (M^+, 100%), 82 (14), 81 (18), 55 (14), 54 (13), 53 (29), and 39 (21) [from 5-(1,2-diaza-1-t-butyl-4-methylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (19), inlet temperature 140—150 °C, pyrolysis time 2 h, inlet residue 0%].

2-t-Butylpyridazin-3(2H)-*ones.*—Pyrolysis of the appropriate 5-(diazapentadienylidene)dioxandione (2 mmol) at 500 °C (10^{-2}—10^{-3} Torr) under the standard conditions gave an acetone solution of the 2-t-butylpyridazinone in the liquid nitrogen trap. The acetone was removed under reduced pressure and the residue was purified by bulb-to-bulb distillation.

The following 2-t-butylpyridazinones were made by this method: *2-t-butylpyridazin*-3(2H)-*one* (42) (0.14 g, 46%), b.p. 134—136 °C (16 Torr), which is apparently hygroscopic, ^{1}H n.m.r. δ ($CDCl_3$) 7.68 (1 H, dd, $^3J_{65}$ 3.5, $^4J_{64}$ 1.8 Hz), 7.10 (1 H, dd, $^3J_{56}$ 3.5, $^3J_{54}$ 9.2 Hz), 6.82 (1 H, dd, $^3J_{45}$ 9.2, $^4J_{46}$ 1.8 Hz), and 1.64 (9 H, s); *m/e* 152 (M^+, 18%), 97 (100), 96 (24), 57 (29), 41 (20), and 39 (18) (Found: C, 58.25; H, 7.85; N, 17.45%; M^+, 152.0955. $C_8H_{12}N_2O{\cdot}2/3H_2O$ requires C, 58.55; H, 8.15; N, 17.05%; M^+, 152.0950) [from 5-(1,2-diaza-1-t-butylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (18), inlet temperature 160—180 °C, pyrolysis time 2 h, inlet residue 9%]: *2-t-butyl-5-methylpyridazin*-3(2*H*)-*one*, (43) (0.19 g, 57%), b.p. 148—150 °C (16 Torr), ^{1}H n.m.r. δ ($CDCl_3$) 7.52 (1 H, d, $^4J_{64}$ 2.0 Hz), 6.58 (1 H, overlapping dq, $^4J_{46}$ 2.0, $^4J_{4,CH3}$ 1.2 Hz), 2.16 (3 H, d, $^4J_{CH_3,4}$ 1.2 Hz), and 1.63 (9 H, s); *m/e* 116 (M^+, 20%), 111 (100), 110 (43), 57 (29), 53 (16), 41 (19), and 39 (11) (Found: C, 65.15; H, 8.7; N, 16.7. $C_9H_{14}N_2O$ requires C, 65.05; H, 8.45; N, 16.85%) [from 5-(1,2-diaza-1-t-butyl-4-methylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (19), inlet temperature 150—160 °C, pyrolysis time 1.5 h, inlet residue 0%].

Pyridazin-3-ones by Gas-phase Decarboxylation of 2,3-Dihydro-3-oxopyridazine-4-carboxylic Acids.—(a) 6-*Methyl*-2-*phenylpyridazin*-3(2H)-*one* (40). 2,3-Dihydro-6-methyl-2-

phenyl-3-oxopyridazine-4-carboxylic acid (30) (0.46 g, 2 mmol) was sublimed at 130—140 °C and 10^{-3} Torr through the furnace tube which was held at 550 °C, during a period of 2 h. The crystalline product was dissolved in methylene dichloride and the latter was subsequently evaporated to give the pyridazinone (40) (0.32 g, 86%), m.p. 75–77 °C (from cyclohexane) (lit.,[33] 79—80 °C).

(b) 6-*Methylpyridazin*-3(2H)-*one* (47). 2-t-Butyl-2,3-dihydro-6-methyl-3-oxopyridazine-4-carboxylic acid (29) (0.42 g, 2 mmol) was sublimed at 100—120 °C and 10^{-2}—10^{-3} Torr through the furnace tube, which was held at 750 °C, during a period of 1 h. Work-up as described in (a) above, gave the pyridazinone (47) (0.19 g, 86%), m.p. 142—143 °C (from cyclohexane) (lit.,[35] 143 °C), ^{1}H n.m.r. δ ($CDCl_3$) 7.12 (1 H, d, $^3J_{54}$ 9.4 Hz), 6.87 (1 H, d, $^3J_{45}$ 9.4 Hz), and 2.30 (3 H, s); *m/e* 110 (M^+, 100%), 82 (23), 81 (23), 54 (15), 53 (50), 52 (10), 51 (15), 41 (20), and 39 (15).

(c) 2-*t-Butyl*-6-*methylpyridazin*-3(2H)-*one* (46). The corresponding pyridazine-4-carboxylic acid (29) (0.28 g, 1.3 mmol) was pyrolysed as described in (b) above, except that the furnace temperature was 500 °C. The pyrolysate was dissolved in methylene dichloride (5 ml) and was extracted with aqueous sodium hydroxide (1M; 2 ml) to remove 2-unsubstituted pyridazinone. The aqueous layer was back-extracted with methylene dichloride (2 × 3 ml) and the combined organic fractions were dried (Na_2SO_4) and concentrated. Bulb-to-bulb distillation of the residue gave the 2-*t-butylpyridazinone* (46) (0.11 g, 50%), b.p. 138—140 °C (16 Torr) as a colourless oil, ^{1}H n.m.r. δ ($CDCl_3$) 6.97 (1 H, d, $^3J_{54}$ 9.2 Hz), 6.71 (1 H, d, $^3J_{45}$ 9.2 Hz), 2.27 (3 H, s), and 1.61 (9 H, s); *m/e* 166 (M^+, 27%) 111 (100), 110 (67), 57 (27), 53 (10), 41 (21), and 39 (10) (Found: C, 64.85; H, 8.7; N, 16.8. $C_8H_{14}N_2O$ requires C, 65.05; H, 8.45; N, 16.85%).

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