An Analysis of the ^{13}C N.M.R. Spectra of Pyridazin-3-ones and Some Specifically Deuteriated Derivatives

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Optimum conditions are reported for the formation of [4-^{2}H]- and [6-^{2}H]-pyridazin-3(2*H*)-ones by gas-phase decarboxylation of the corresponding [^{2}H]carboxylic acids or by cyclisation of the appropriate [*N*-^{2}H]- or [3-^{2}H]-5-(1,2-diazabutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione. By the use of deuteriated derivatives, the ^{13}C n.m.r. parameters of pyridazin-3(2*H*)-one are assigned as follows: C(3), δ 164.00 ($^3J_{CH}$ 8.6 Hz); C(4), δ 130.45 ($^1J_{CH}$ 171.9, $^3J_{CH}$ 6.1 Hz); C(5), δ 134.71 ($^1J_{CH}$ 168.3, $^2J_{CH(6)}$ 8.0 Hz); C(6), δ 139.02 ($^1J_{CH}$ 188.9, $^2J_{CH}$ 2.7, $^3J_{CH(4)}$ 7.9 Hz). Chemical shifts and coupling constants of a range of *C*-methyl-, *N*-t-butyl-, and *N*-aryl-pyridazin-3(2*H*)-ones are reported, and the substituent effects are correlated with model systems.

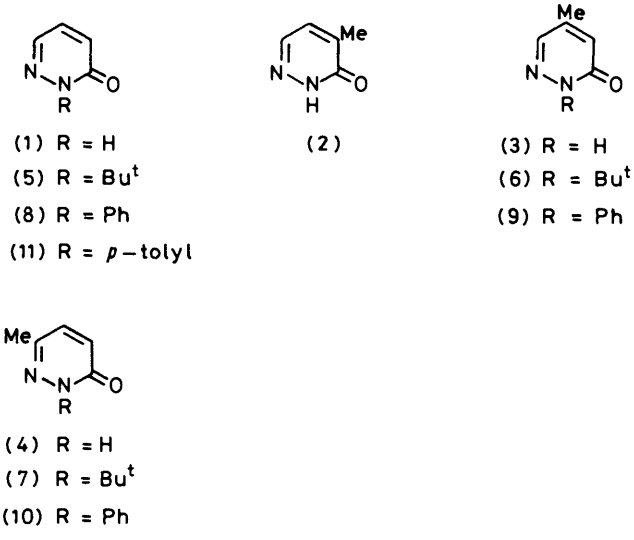
The present paper reports a comprehensive analysis of the ^{13}C n.m.r. spectra of the pyridazin-3(2*H*)-one system (1), and its *C*-alkyl (2)—(4), *N*-alkyl (5)—(7), and *N*-aryl (8)—(11) derivatives. No such study of any pyridazinones has been reported, and at an early stage of the investigation it became apparent that *C*-deuteriated derivatives were needed for a complete and unambiguous analysis of the spectra. Literature precedence for such compounds is again sparse: the 5-mono- and 5,6-di-deuteriated compounds are formed by electrophilic deuteriation of the parent system,[1] and one tritiated derivative of a heavily substituted pyridazinone has been reported.[2] Our earlier synthesis [3] (Scheme 1) was therefore modified to provide pyridazinones specifically labelled at the 4-(or 6-)positions.

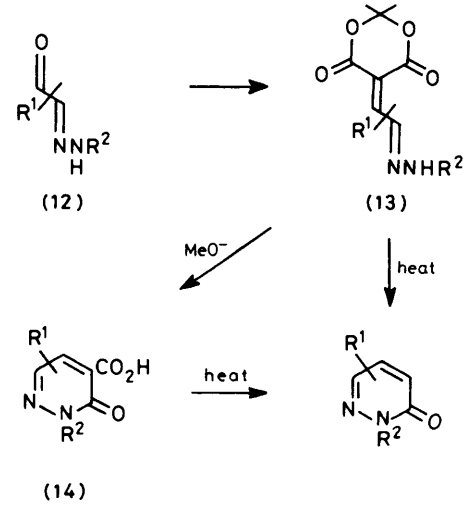
In theory, the formation of [4-^{2}H]-derivatives by the Meldrum's acid route (Scheme 1) requires simple exchange of the H in the NH of compound (13) or in the OH of (14) with deuterium, followed by gas-phase cyclisation or decarboxylation, respectively. In practice, trial experiments with (13; R^1 = H, R^2 = Bu^t) using exchange with deuterium oxide and conventional work-up gave the [4-^{2}H]-compound exclusively, but the incorporation was disappointing (*ca.* 60%), owing to back-exchange during manipulation. Better results (>80% incorporation) were obtained by dissolving the precursor in excess of methan[^{2}H]ol *within the inlet system*, followed by evaporation of the solvent and pyrolysis in the usual way. However the optimum conditions involved pyrolysis in a stream of deuterium oxide *in addition* to the methan[^{2}H]ol treatment (see Experimental section). By this means the [4-^{2}H]-derivatives of (1) and of (10) were made with 92% and 91% deuterium incorporation, respectively.

Surprisingly, the 5-methylpyridazinone (3) obtained by a similar method from (15) showed only 68% incorporation at the 4-position, but, in addition, a significant amount of the label had migrated to the methyl group. The migration probably takes place at an early stage in the reaction sequence since cyclisation at a higher temperature showed the same amount of migration, and combined decarboxylation–debutylation of the [^{2}H]carboxylic acid (14; R^1 = 5-Me, R^2 = Bu^t) gave the [4-^{2}H]pyridazinone with high specificity (92% incorporation). The mechanism proposed in Scheme 2 accounts for these observations.

The 4-methyl derivative (2), which is not available by the route of Scheme 1, was prepared by gas-phase decarboxylation [4] of the 6-carboxylic acid (16).[5,6] Brown's conditions [4] for decarboxylation of an indole derivative were used without further optimisation. The [6-^{2}H]-derivative of (2) was obtained by decarboxylation of the [^{2}H]carboxylic acid (16).

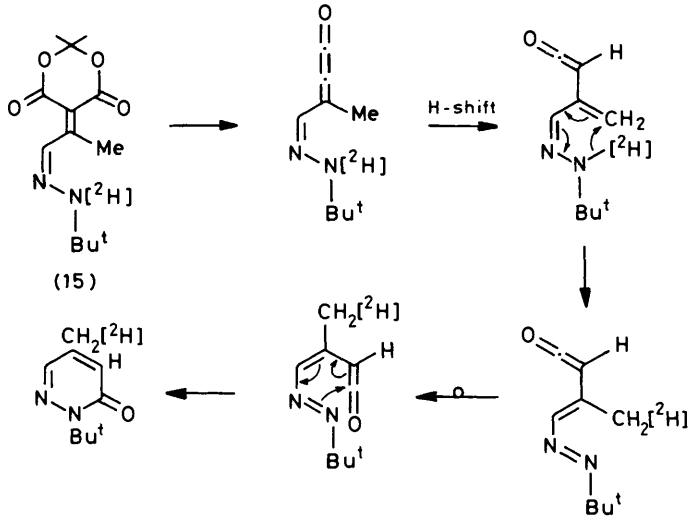
In order to prepare the [6-^{2}H]-derivative of (1), the known





Scheme 1.

properties [7] of the t-butylhydrazone precursor (12; R^1 = H, R^2 = Bu^t) were employed. Deuterium exchange at the carbon atom of the hydrazone function takes place under basic



Scheme 2.

conditions and the isolated [2-^{2}H]hydrazone was treated with Meldrum's acid to give the condensation product (13; R^1 = H, R^2 = Bu^t). Unfortunately, a variable amount of scrambling (up to 25%) of label between the 5-[C(3)] and 5-[C(4)] positions of this compound took place. The mechanism of this scrambling reaction remains obscure, though a series of control experiments has eliminated possible equilibration of [2-^{2}H]- and [1-^{2}H]-hydrazones under the conditions of the reaction (see Experimental section). The results strongly suggest that the scrambling takes place during the course of the condensation. In general, [6-^{2}H]pyridazinones are probably best made, as above, from the carboxylic acids, but in the present case, the incorporation was sufficient for an unambiguous analysis of the spectra (see below).

The ^{13}C n.m.r. chemical shifts of the pyridazinones (1)—(11) are given in Table 1. [$^2H_4$]Methanol was chosen as the solvent for the study, because of its volatility, and because of the low solubility of certain members of the series in alternative solvents (*e.g.* [^{2}H]chloroform).

In the spectrum of pyridazin-3(2*H*)-one (1) itself, the only signal which could be assigned by inspection was that of the carbonyl C(3), at 164.00 p.p.m.: the other resonances occurred in the range 130—140 p.p.m. The spectra of the [4-^{2}H]- and [6-^{2}H]-derivatives of (1) showed marked reductions in the intensities of the peaks at δ 130.45 and 139.02, respectively, which also allowed the remaining methine signal (at δ 134.71) to be assigned as that due to C(5). The sequence δ(4) < δ(5) < δ(6) is also followed in the signals due to the methyl carbon atoms in compounds (2)—(4). The resonances due to the ring carbon atoms of (2) and (3) were assigned unambiguously, as above, using [6-^{2}H]- and [4-^{2}H]-derivatives, respectively, and those of the remaining compounds were assigned by analogy. In certain cases in the 2-phenyl series (8)—(10), peaks with closely similar chemical shift were distinguished by the characteristic multiplicities of the pyridazinone carbon signals in the fully coupled spectra (see below). For example, the peaks due to C(4) and to the *p*-carbon of the phenyl ring of the pyridazinones (9) and (10) are separated by 2 p.p.m. or less, but the characteristic doublet of quintets due to C(4) which is present in all the 5-methyl compounds (3), (6), and (9) and the characteristic simple doublet due to C(4) which is present in the 6-methyl compounds (4), (7), and (10), enabled the ambiguities to be resolved.

Full assignment of the peaks has allowed the calculation of

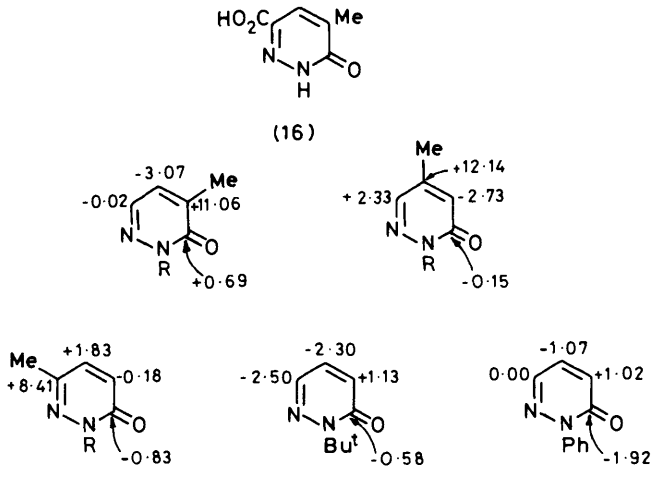


Figure. Substituent effects for *C*-methyl-, *N*-t-butyl-, and *N*-phenyl-pyridazin-3(2*H*)-ones [positive values indicate δ (derivative) > δ (parent): errors are ±0.3 p.p.m.]

the substituent effects shown in the Figure. Although the range of compounds is small [especially for the 4-methyl derivative(s)], the data show good consistency. *C*-Methyl substitution causes the expected large shift to high frequency of the signal due to the substituted carbon atom. The adjacent carbon atoms are shifted to low and to high frequency where these are connected to the substituted atom by a formal double and a formal single bond, respectively. This behaviour is similar in direction, but smaller in magnitude to that due to corresponding substitution in alkenes.[8] Shifts at the other carbon atoms are small and to low frequency.

The direction (but not the magnitude) of the shifts due to *N*-substitution are broadly independent of the nature of the substituent. These effects cannot therefore be solely due to electron-density factors, since the t-butyl and phenyl groups would be expected to act in opposite directions in this case.

The one-bond coupling constants associated with the ring carbon atoms (Tables 2 and 3) fall in the range expected for nitrogen heterocycles.[9] In particular, the high value of $^1J_{C(6),H(6)}$ is typical for methine groups adjacent to nitrogen.

Table 1. ^{13}C N.m.r. spectra (20 MHz) of pyridazinones (1)—(11) [a]

Compound	δ(3)	δ(4)	δ(5)	δ(6)	δ(Other)	
(1)	164.00	130.45	134.71	139.02		
(2)	164.69	141.51	131.64	139.00	4-Me	15.92
(3)	163.98	127.69	147.03	141.46	5-Me	18.41
(4)	163.17	130.19	136.64	147.55	6-Me	20.32
(5)	163.45	131.43	132.64	136.71	2-Bu^t	28.02
						66.58
(6)	163.31	128.88	144.56	138.93	5-Me	17.51
					2-Bu^t	28.11
						66.07
(7)	162.66	131.42	134.29	144.89	6-Me	20.72
					2-Bu^t	28.10
						66.05
(8)	162.18	131.51	133.69	139.06	2-Ph [b]	142.76
						126.65
						129.73
						129.44
(9)	161.90	128.65	145.88	141.39	5-Me	18.11
					2-Ph [b]	142.61
						126.59
						129.68
						129.28
(10)	161.32	131.24	135.59	147.58	6-Me	20.64
					2-Ph [b]	142.86
						126.69
						129.67
						129.24
(11)	162.16	131.38	133.55	138.93	2-Ar [b]	140.31 [c]
						126.38
						130.21
						139.60 [c]
					p-Me	21.09

[a] Recorded for solutions in [$^2H_4$]methanol. [b] Peaks quoted in the order C(α), C(*o*), C(*m*), C(*p*). [c] Assigned by analogy with the spectrum of (8).

Table 2. Carbon–proton coupling constants (J_{CH}) for pyridazin-3(2*H*)-one and its *C*-methyl derivatives [a]

Compd.	C(3)		C(4)		C(5)		C(6)		C(Me)	
(1) [b]	$^3J_{CH}$	8.6	$^1J_{CH}$	171.9	$^1J_{CH}$	168.3	$^1J_{CH}$	188.9		
			$^3J_{CH(6)}$	6.1	$^2J_{CH(6)}$	8.0	$^2J_{CH(5)}$	2.7		
							$^3J_{CH(4)}$	7.9		
(2) [c]	$^3J_{CH(5)}$	8.24	$^2J_{CH(Me)}$	6.54	$^1J_{CH}$	164.40	$^1J_{CH}$	186.59	$^1J_{CH}$	128.9 [b]
	$^3J_{CH(Me)}$	4.12	$^3J_{CH(6)}$	6.54	$^2J_{CH(6)}$	8.02	$^2J_{CH(5)}$	2.92	$^3J_{CH(5)}$	5.0 [b]
	$^4J_{CH(6)}$	0.90	$^2J_{CH(5)}$	0.95	$^3J_{CH(Me)}$	5.49	$^4J_{CH(Me)}$	0.76		
(3) [c]			$^1J_{CH}$	168.23	$^2J_{CH(Me)}$	6.61	$^1J_{CH}$	186.45	$^1J_{CH}$	128.85
			$^3J_{CH(Me)}$	5.39	$^2J_{CH(6)}$	6.61	$^3J_{CH(Me)}$	4.90	$^3J_{CH(4)}$	4.48
			$^3J_{CH(6)}$	5.39			$^3J_{CH(4)}$	6.50	$^3J_{CH(6)}$	2.17
(4) [c]	$^3J_{CH(5)}$	8.88	$^1J_{CH}$	170.74	$^1J_{CH}$	165.65	$^2J_{CH(Me)}$	7.30	$^1J_{CH}$	128.49
	$^2J_{CH(4)}$	1.38			$^3J_{CH(Me)}$	3.61	$^2J_{CH(5)}$	2.58	$^3J_{CH(5)}$	1.55 [d]
							$^3J_{CH(4)}$	7.30		

[a] Values are given in Hz for solutions in [$^2H_4$]methanol. [b] Recorded at 20 MHz. [c] Recorded at 90 MHz. [d] Assigned by analogy.

The spectrum of the parent compound (1) shows, in addition, long range couplings from C(3), C(4), C(5), and C(6) to one, one, one, and two protons, respectively. No change was observed when the spectrum was recorded using [$^1H_4$]-methanol as solvent, and so coupling due to the NH is small in this series. Minor couplings were assigned using the [4-^{2}H]- and [6-^{2}H]-derivatives of (1). Thus the doublet due to C(3) was unchanged in the spectra of both these compounds, and so the minor coupling is due to H(5). In contrast, the signals due to C(4) and C(5) of the [6-^{2}H]-derivative are both clean doublets, and therefore the minor coupling is due to H(6) in both cases. The larger of the two long-range couplings from C(6) is removed in the spectrum of the [4-^{2}H]-derivative. It is therefore three-bond couplings which are most significant for C(3), C(4) and C(6), and only C(5) shows a two-bond coupling of a size greater than 3 Hz. Similar trends in the ring coupling constants are observed in the *C*-methyl and *N*-substituted derivatives (Tables 2 and 3).

Although the spectra of the methyl derivatives (2)—(4) were more complex due to long-range coupling to the substituent, highly resolved first-order spectra were obtained at 90 MHz. Assignment of the methine resonances was unambiguous by inspection, while the couplings at the quaternaries and at the methyl group, were analysed using deuteriated derivatives, or by analogy with (1). Thus, to take compound (2) as an example, the quaternary C(4) occurs as a

Table 3. Available carbon–proton coupling constants (J_{CH}) for *N*-substituted pyridazin-3(2*H*)-ones [a]

Compd.	C(3)		C(4)		C(5)		C(6)		C(Me)	
(5)	$^3J_{CH(5)}$	8.5	$^1J_{CH}$	171.0	$^1J_{CH}$	168.7	$^1J_{CH}$	188.8		
			$^3J_{CH(6)}$	6.1	$^2J_{CH(6)}$	7.8	$^2J_{CH(5)}$	3.0		
							$^3J_{CH(4)}$	8.4		
(6)			$^1J_{CH}$	166.9		*b*	$^1J_{CH}$	187.5	$^1J_{CH}$	128.0
			$^3J_{CH(Me)}$	5.4			$^3J_{CH(Me)}$	5.5	$^3J_{CH(4)}$	4.8
			$^3J_{CH(6)}$	5.4			$^3J_{CH(4)}$	5.5	$^3J_{CH(6)}$	1.7
(7)	$^3J_{CH(5)}$	8.5	$^1J_{CH}$	170.1	$^1J_{CH}$	166.4		*b*	$^1J_{CH}$	128.3
					$^3J_{CH(Me)}$	3.3				
(8)	$^3J_{CH(5)}$	8.9	$^1J_{CH}$	172.6	$^1J_{CH}$	169.8	$^1J_{CH}$	189.4		
			$^3J_{CH(6)}$	6.1	$^2J_{CH(6)}$	7.6	$^2J_{CH(5)}$	3.0		
							$^3J_{CH(4)}$	8.6		
(9)			$^1J_{CH}$	168.5		*b*	$^1J_{CH}$	*ca.* 188 [c]	$^1J_{CH}$	128.8
			$^3J_{CH(Me)}$	5.7			$^3J_{CH(Me)}$	5.7	$^3J_{CH(4)}$	4.8
			$^3J_{CH(6)}$	5.7			$^3J_{CH(4)}$	5.7	$^3J_{CH(6)}$	1.5
(10)	$^3J_{CH(5)}$	9.0	$^1J_{CH}$	171.9	$^1J_{CH}$	167.7		*b*	$^1J_{CH}$	128.6
	$^2J_{CH(4)}$	1.6			$^3J_{CH(Me)}$	3.4				

[a] Values are given in Hz, obtained from spectra recorded at 20 MHz for solutions in [$^2H_4$]methanol; minor couplings are assigned by analogy with those in Table 2; Bu^t and Ph carbon resonances were not analysed. [b] Complex at 20 MHz. [c] Confused by overlapping signals at 20 MHz.

quintet of doublets, but as a broad quartet in the spectrum of its [6-^{2}H]-derivative. These results are interpreted as being due to approximately equal coupling between C(4) and H(6), and C(4) and the methyl group, with a small coupling (<1 Hz) to H(5), which was not resolved in the spectrum of the deuteriated compound. Similarly, the signal due to the methyl group occurs as a quartet of doublets in both the parent compound (2) and its [6-^{2}H]-derivative, and so the minor coupling is due to H(5). Alternatively, the signal due to C(3) of the [6-^{1}H]-compound was a complex sextet of doublets. If the expected three-bond coupling of *ca.* 8 Hz to C(5) is assumed, the remaining couplings must be due to the methyl group (*ca.* 4 Hz) and C(6) (<1 Hz). The spectra of compounds (3) and (4) were assigned similarly (Table 2), and the spectra of the *N*-substituted derivatives (5)—(10) (Table 3) were assigned by analogy with their NH analogues.

In general, two-bond coupling constants from the ring carbon atom to the methyl substituent are in the range 6—8 Hz, and three-bond couplings from the site adjacent to the substituent are in the range 3—6 Hz. Only three-bond coupling from the methyl carbon atom to the ring protons was detected in compounds (2) and (3) and their deuteriated analogues, and so the small coupling in (4) (*ca.* 1 Hz) was assigned by analogy. It is of interest that the carbonyl C(3) in the 4- and 6-methylpyridazinones (2) and (4) show a small coupling (resolved at 90 MHz) to H(6) and H(4), respectively. These are not resolved in the spectrum of the 5-methyl compound (3), where the carbonyl resonance appears as a broad singlet.

Experimental

Unless otherwise stated, ^{1}H, ^{2}H, and ^{13}C n.m.r. spectra were recorded at 100, 55, and 20 MHz, respectively.

Preparation of Pyridazin-3-ones.—These compounds were prepared as previously described,[3] with the sole exception of the 4-methyl derivative (2) for which the route is inapplicable. This material was therefore made by gas-phase decarboxylation of 2,3-dihydro-4-methyl-3-oxopyridazine-6-carboxylic acid [5] as follows: a sample of the acid (0.31 g, 2 mmol) was sublimed at 180—200 °C and 10^{-2} Torr during 80 min, through an empty silica furnace tube (35 × 2 cm) whose temperature was maintained at 850 °C. The solid pyrolysate was worked up as previously described [3] to give crude 4-methylpyridazin-3(2*H*)-one (0.17 g, 77%), m.p. 153—155 °C (from benzene) (lit.,[5] 158—159 °C), δ($CDCl_3$) 7.72 (1 H, d, $^3J_{5,6}$ 3.8 Hz), 7.09 (1 H, d of q, $^3J_{5,6}$ 3.8, $^4J_{5,CH_3}$ 1.2 Hz), and 2.20 (3 H, d, $^4J_{CH_3,5}$ 1.2 Hz); *m/e* 110 (M^+, 100%), 81 (43), 53 (67), and 39 (33).

Preparation of [4-^{2}H]*Pyridazin-3-ones.*—The appropriate 5-(1,2-diazabutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione or 2,3-dihydro-3-oxopyridazine-4-carboxylic acid was placed in a test tube which was equipped with a B24 ' Quickfit ' cone and had a capillary side-arm (B10 cone) adjacent to the ground glass joint. The solid was dissolved in the stated quantity of hot methan[^{2}H]ol, which was then evaporated *in situ* at 10^{-1} Torr. After the introduction of dry nitrogen, a flask containing deuterium oxide (*ca.* 2 ml) was attached to the capillary side-arm, and the entire assembly was attached to the furnace tube, to form the inlet system of the pyrolysis apparatus. The deuterium oxide remained *outside* the inlet heater: under typical f.v.p. conditions of 10^{-2}—10^{-3} Torr, it evaporated at a rate of 20—50 mmol h^{-1}, and was collected along with volatile products in the cold trap at the exit point of the furnace. Work-up conditions were as previously described.[3] The deuterium incorporation was measured by ^{1}H n.m.r.

The following derivatives were made by this method: [4-^{2}H]pyridazin-3(2*H*)-one (0.09 g, 94%), *m/e* 97 (M^+, 100%) {from 5-(1,2-diaza-1-t-butylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione (0.26 g, 1 mmol) and methan-[^{2}H]ol (2 ml) inlet temperature 190 °C, furnace temperature 750 °C, pyrolysis time 30 min}, deuterium incorporation at the 4-position = 92%; [4-^{2}H] 5-methylpyridazin-3(2*H*)-one (0.04 g, 85%), *m/e* 111 (M^+, 100%), {from 2,3-dihydro-5-methyl-3-oxo-2-t-butylpyridazine-4-carboxylic acid (0.09 g, 0.43 mmol) and methan[^{2}H]ol (1 ml), inlet temperature 120 °C, furnace temperature 750 °C, pyrolysis time 15 min}, deuterium incorporation at 4-position = 92%. {In an attempt to make this compound directly from the Meldrum's acid derivative (15) (0.54 g, 2 mmol) and methan[^{2}H]ol (5 ml), the 5-methylpyridazin-3-one (0.20 g, 90%) which was obtained by pyrolysis (750 °C, 1 h) showed deuterium incorporation at the 4-position of only 68%, and at the methyl group of 13%. The ^{2}H n.m.r. spectrum showed two significant peaks at δ 6.76 and 2.21 corresponding to the 4-^{2}H and the methyl-^{2}H

respectively. The ratios were unchanged (^{1}H n.m.r.) when the pyrolysis was carried out at 850 °C.} [4-^{2}H]-6-Methyl-2-phenylpyridazin-3(2*H*)-one was prepared on a 0.5-mmol scale from 5-(1,2-diaza-3-methyl-1-phenylbutadien-4-ylidene)-2,2-dimethyl-1,3-dioxan-4,6-dione and methan[^{2}H]ol (4 ml) (inlet temperature 150 °C, furnace temperature 550 °C, pyrolysis time 15 min), deuterium incorporation at the 4-position = 91%.

4-*Methyl*[6-^{2}H]*pyridazin*-3(2H)-*one*.—The corresponding 6-carboxylic acid [5] (0.2 g, 1.3 mmol) was dissolved in hot deuterium oxide (9 ml), in the modified inlet system (see above). The solvent was then evaporated under reduced pressure and the residue was pyrolysed at 850 °C and 10^{-2} Torr during 1 h (inlet temperature 180—200 °C) in a deuterium oxide stream as described above. The crude pyridazinone (0.120 g), *m/e* 111 (M^+, 100%) was obtained by standard work-up, and was used without purification. The deuterium incorporation was 81%.

l6-^{2}H]*Pyridazin*-3(2H)-*one*.—(*a*) [2-^{2}H]*Glyoxal mono-t-butylhydrazone*. The hydrazone (0.32 g, 2.5 mmol) was added to a solution of sodium methoxide [from sodium (*ca.* 10 mg, 0.5 mmol)] in methan[^{2}H]ol (5 ml) and the reaction was monitored by ^{1}H n.m.r. spectroscopy. The experiment was repeated twice using sodium (9.1 mg and 13.1 mg), and the times required for *ca.* 70% exchange were 23 and 8 h, respectively. Most of the solvent was removed at room temperature and 10^{-1} Torr, and deuterium oxide (5 ml) was added to the residue. The mixture was extracted with methylene dichloride (3 × 15 ml), and the organic extracts were dried (Na_2SO_4), concentrated and flash distilled at 120 °C (16 Torr), to give the [2-^{2}H]hydrazone (0.17 g, 53%). Deuterium incorporation = 70%.

(*b*) 5-(1-t-*Butyl*[3-^{2}H]-1,2-*diazabutadien*-4-*ylidene*)-2,2-*dimethyl*-1,3-*dioxan*-4,6-*dione*. A solution of the above hydrazone (0.18 g, 1.5 mmol) and 2,2-dimethyl-1,3-dioxan-n.m.r. spectrum of the product. Perhaps coincidentally, the former product was derived from a reaction in which 2,2-dimethyl-[5,5-$^2H_2$]-1,3-dioxan-4,6-dione was used. (No deuterium was incorporated in the product from this material and undeuteriated glyoxal t-butylhydrazone.)

In an attempt to discover the origin of the scrambling, a solution of the hydrazone (21 mg, 0.16 mmol), piperidine (1 µl), acetic acid (1 µl), and water (1 µl) in [$^2H_6$]benzene (0.3 ml) was monitored by ^{1}H n.m.r. No scrambling took place during 24 h. Addition of the dione (10 mg, 0.07 mmol) caused *no* scrambling in the residual hydrazone over a further 20 h. However, the isolated condensation product showed two peaks in the ^{2}H n.m.r. spectrum [δ($CHCl_3$) 8.54 and 8.24 (integral ratio 6.4 : 1)], which implies that the scrambling takes place during the course of the condensation.

(*c*) [6-^{1}H]*Pyridazin*-3(2H)-*one*. The product from part (*b*) (0.26 g, 1 mmol) was dissolved in hot methan[^{1}H]ol (2 ml) within the inlet tube. The solvent was evaporated under reduced pressure and the residue was sublimed at 160—170 °C and 10^{-2} Torr through the furnace tube (furnace temperature 750 °C, pyrolysis time 35 min). Standard work-up gave the pyridazinone (0.07 g, 73%), *m/e* 97 (100%), deuterium incorporation at 6-position = 72%, deuterium incorporation at 5-position (through scrambling in the formation of the precursor) = 13%.

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