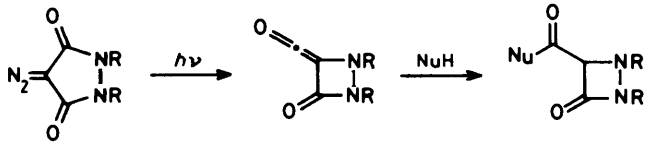
Regioselectivity in the Photochemical Ring Contraction of 4-Diazopyrazolidine-3,5-diones to give Aza-β-lactams

Geoffrey Lawton
Roche Products Ltd., P.O. Box 8 Welwyn Garden City, Hertfordshire AL7 3AY
Christopher J. Moody,* Christopher J. Pearson, and David J. Williams
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

Irradiation of 4-diazopyrazolidine-3,5-diones (**15**) in the presence of alcohols or water gave mixtures of the isomeric 1,2-diazetidinones (**16**) and (**17**), formed by competing photochemical Wolff rearrangement of the two nitrogen groups, followed by reaction of the resulting ketenes with the nucleophile. Some regioselectivity is observed in the ring contraction process, and the relative order of migration of nitrogen groups is NPh > $NCHPh_2$ ~ NCH_2Ph ~ NMe > NCH_2CO_2Et. The structures of the 1,2-diazetidinones (**17c**) and (**24**) were confirmed by *X*-ray crystallography, and a crystal structure of the diazo compound (**15g**) was also obtained. Possible reasons for the regioselectivity in the ring contraction are discussed.

In the preceding paper we reported the details of a new route to 1,2-diazetidinones, aza analogues of β-lactams, based on the photochemical ring contraction of symmetrically substituted 4-diazopyrazolidine-3,5-diones in the presence of a nucleophile (Scheme 1).[1] The success of this reaction demonstrated that despite the participation of the nitrogen lone pair in amide resonance, the nitrogen atom would migrate to the electron deficient centre to effect the desired ring contraction. In general N–C bonds show a marked reluctance to migrate in the photochemical Wolff rearrangement,[2] and only a few examples are known.[3]

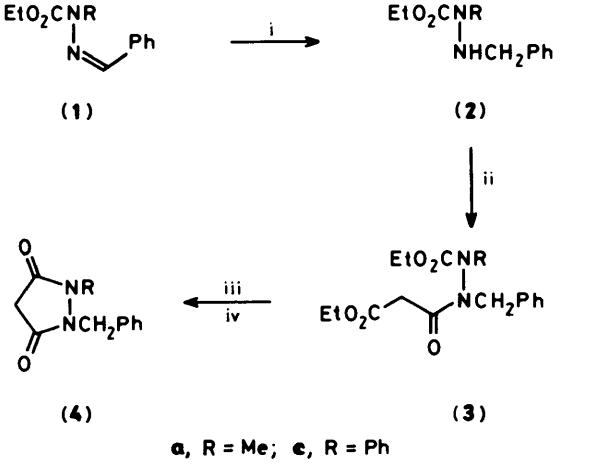


Scheme 1. R = $PhCH_2$, Pr, or RR = $(CH_2)_4$; Nu = EtO, Bu^{t}O, Et_2N or HO

We have now investigated this reaction in more detail with a view to determining the electronic and steric requirements for nitrogen atoms to migrate in the Wolff rearrangement, and to extending the range of aza-β-lactams available by this route. Our results on the photochemical ring contraction of unsymmetrically substituted 4-diazopyrazolidine-3,5-diones are reported in detail herein.[4]

Results and Discussion

Preparation of 4-Diazopyrazolidine-3,5-diones.—Eight mono- and bi-cyclic unsymmetrical 4-diazopyrazolidine-3,5-diones (**15**) were prepared, containing a range of substituents. The choice of substituents bearing carboxylate groups is influenced by the fact that any potential β-lactam analogue would almost certainly require such a substituent. The 2-methyl- and 2-phenyl-1-benzylpyrazolidine-3,5-diones (**4a,c**) were prepared by a similar route to that already used for the symmetrical 1,2-dialkyl derivatives.[1] Thus the ethyl benzylidenecarbazates (**1a**), prepared by methylation of ethyl benzylidenecarbazate itself, and (**1c**), prepared by acylation of benzaldehyde phenylhydrazone, were hydrogenated to give the corresponding benzyl derivatives (**2**). Acylation of (**2**) with ethoxycarbonylacetyl chloride followed by base mediated cyclisation, hydrolysis and decarboxylation gave the pyrazolidine-3,5-diones (**4a,c**) (Scheme 2).

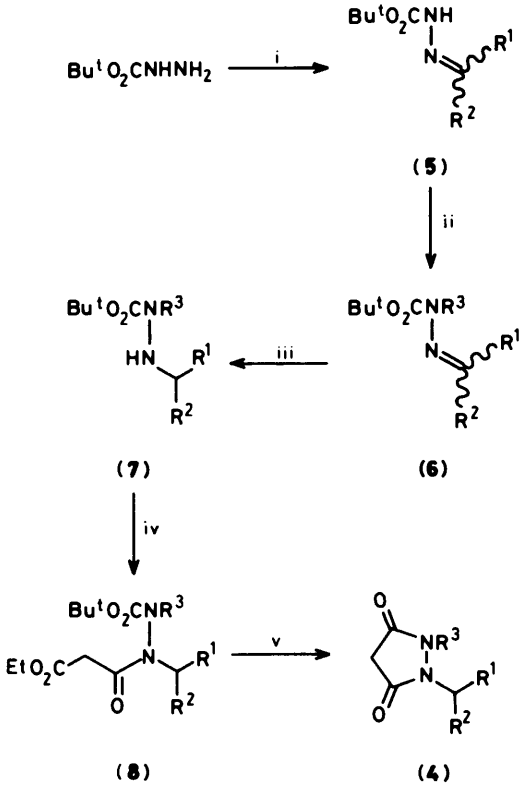


Scheme 2. *Reagents:* i, H_2, Pd–C, EtOH; ii, EtO_2CCH_2COCl, Et_3N, C_6H_6; iii, NaOEt, EtOH; iv, H_2O, MeCN, reflux

Although the sodium ethoxide cyclisation worked well for the simple alkyl and aryl substituted pyrazolidinediones, it seemed likely that problems would arise when other functional groups such as esters were present, and therefore an alternative route to pyrazolidinediones was developed (Scheme 3).

Condensation of t-butyl carbazate with aldehydes or ketones gave the expected t-butyloxycarbonylhydrazones (**5**), which were readily alkylated to give the hydrazones (**6**). Reduction of the C=N bond by catalytic hydrogenation or by sodium cyanoborohydride gave the hydrazines (**7**), which were acylated with ethoxycarbonylacetyl chloride, and then cyclised by treatment with trifluoroacetic acid (TFA). The pyrazolidinediones (**4b**), (**4d**), and (**4f**) were prepared by this route. The intermediate hydrazine (**7c**) was obtained from the known[5] Bu^tO_2-$CNHNHCH_2CO_2Et$ by acylation with benzyl chloroformate, methylation, and removal of the benzyloxycarbonyl group by hydrogenolysis.

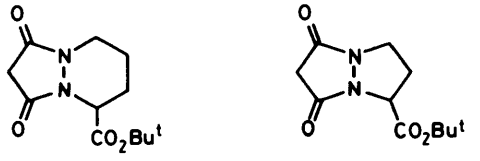
Although the ring contraction of bicyclic 4-diazopyrazolidinediones had already been found to be less satisfactory than in the



(4)	(5)–(8)	R^1	R^2	R^3
b	a	Ph	Ph	Me
d	b	Ph	H	CH_2CO_2Et
e	c	H	CO_2Et	Me
f	d	Ph	CO_2CH_2Ph	Me

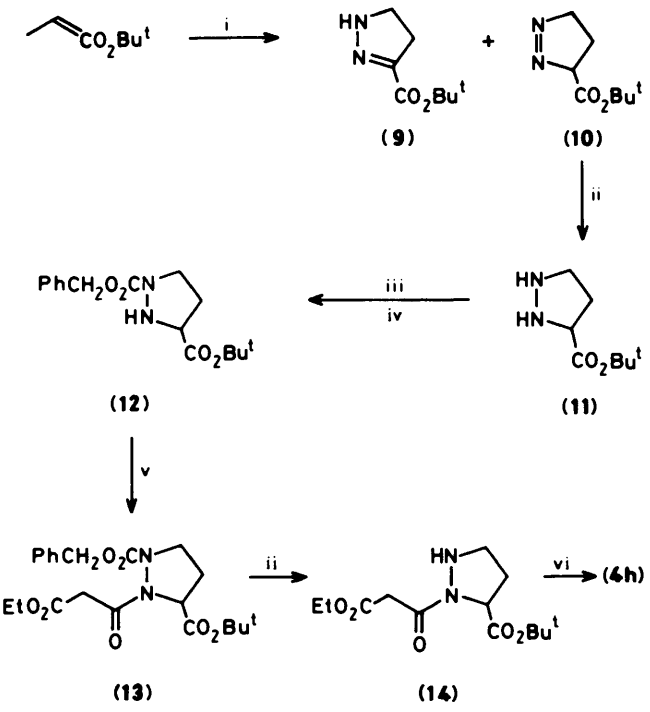
Scheme 3. *Reagents:* i, R^1R^2CO, EtOH; ii, R^3X, K_2CO_3, acetone; iii, H_2, Pd–C, EtOH or $NaBH_3CN$, THF, H^+; iv, EtO_2CCH_2COCl, Et_3N, C_6H_6; v, TFA, CH_2Cl_2. [*Note.* (**7c**) was prepared differently—see text.]

monocyclic series,[1] an investigation into unsymmetrical bicyclic compounds was still considered worthwhile, and therefore the preparation of the precursor pyrazolidinediones (**4g**) and (**4h**) was undertaken.



(**4g**) (**4h**)

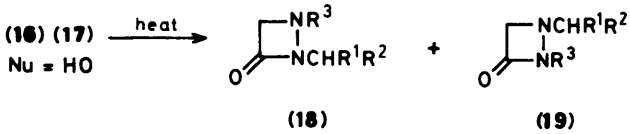
Fortunately the pyrazolopyridazine derivative (**4g**) was readily available from other work,[6] and a similar route was used to prepare the five-membered ring analogue (**4h**) (Scheme 4). Cycloaddition of diazomethane to t-butyl acrylate gave the 4,5-dihydropyrazole (**9**) as the major product, together with some of the required azo compound (**10**). Since the rearrangement of (**10**) into (**9**) was sufficiently slow, immediate catalytic hydrogenation of the reaction mixture resulted in the reduction of (**10**) to the cyclic hydrazine (**11**). When the mixture of (**9**) and (**11**) was acylated with benzyl chloroformate, selective reaction of N-1 of (**11**) occurred to give, after chromatographic separation of the unwanted (**9**), the pyrazolidine (**12**) in 18% overall yield. Acylation of (**12**) with ethoxycarbonylacetyl chloride, followed by hydrogenolysis of the benzyloxycarbonyl group gave (**14**), which was cyclised to (**4h**) under basic conditions.



Scheme 4. *Reagents:* i, CH_2N_2, ether; ii, H_2, Pd–C, EtOH; iii, $PhCH_2OCOCl$; iv, chromatography; v, EtO_2CCH_2COCl, Et_3N, Et_2O; vi, NaOEt, EtOH, reflux

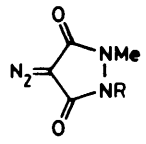
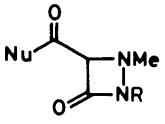
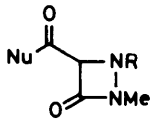
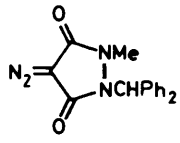
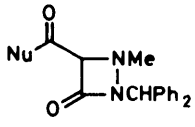
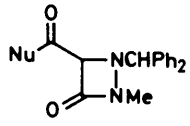
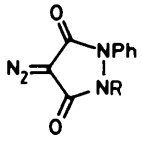
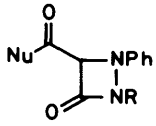
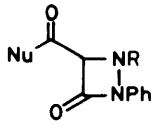
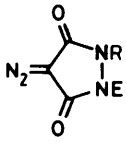
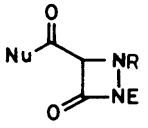
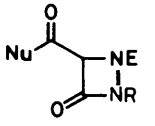
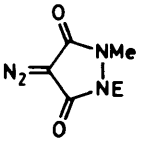
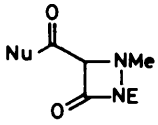
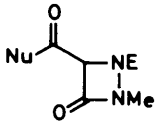
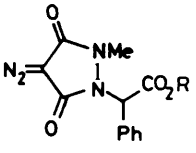
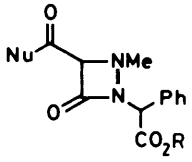
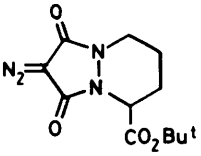
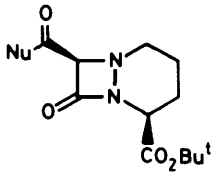
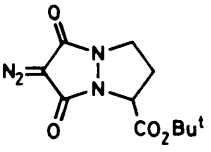
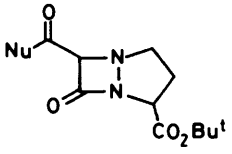
The pyrazolidinediones (**4**) were converted into the corresponding 4-diazo derivatives (**15**) under standard conditions using tosyl azide as diazo-transfer reagent.

Photochemical Ring Contraction Reactions.—The 4-diazopyrazolidine-3,5-diones (**15**) were irradiated in ether in the presence of a nucleophile such as methanol, ethanol, or water, to give mixtures of the diazetidinones (**16**) and (**17**). The results are summarised in Table 1. The ratio of the four-membered ring products was determined by integration of the appropriate signals in the ^1H n.m.r. spectra of the mixtures. The assignment of signals corresponding to the diazetidinones (**16**) and (**17**) was confirmed by chromatographic separation of the regioisomers as their esters, obtained directly from photolysis in the presence of alcohols, or as the 4-unsubstituted compounds (**18**) and (**19**) obtained by decarboxylation[1] of the corresponding carboxylic acids (**16**) and (**17**) (Nu = HO). In general it was assumed that



(18),(19)	R^1	R^2	R^3
a	Ph	Ph	Me
b	H	Ph	Ph
c	Ph	H	CH_2CO_2Et
d	CO_2Bu^t—CH—	$(CH_2)_3$—	

Table 1. Photochemical ring contraction of 4-diazopyrazolidine-3,5-diones (R = $PhCH_2$, E = EtO_2CCH_2)

	Diazo compound (15)	Diazetidinone (16)	Diazetidinone (17)	NuH	Yield (%)	Ratio [(16):(17)]
a				EtOH	30	1:1
				HOH	33	1:1
b				EtOH	36	1:1
				HOH	33	1:1
c				EtOH	72	1.7:1
				HOH	55	1.6:1
d				MeOH		2.5:1[a]
				HOH	47	2.8:1
e				MeOH		2:1[a]
f			—	HOH	0	
g			—	EtOH	12	>10:1
				HOH	14	>10:1
				b	11	>10:1
h			—	EtOH	0	

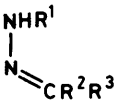
[a] Isomeric mixture could not be obtained pure; ratio from ^1H n.m.r. [b] Photolysis carried out in dry ether; see text.

protons on a substituent attached to N-2 would resonate at lower field than if the same substituent were on N-1.

The initial results with respect to regioselectivity were disappointing, *N*-methyl, *N*-benzyl, and *N*-benzhydryl groups having similar migratory aptitudes and leading to 1:1 mixtures of the regioisomeric diazetidinones (**16**) and (**17**). However, in the photolysis of (**15c**) the *N*-phenyl substituent shows a slight preference to migrate over the *N*-benzyl group to give the 2-benzyl-1-phenyl-diazetidinone (**16c**) as the major product. The structure of the minor product from the photolysis in the presence of ethanol, ethyl 1-benzyl-2-phenyl-3-oxodiazetidine-4-carboxylate (**17c**; Nu = EtO) was confirmed by its indepen-

dent synthesis,[7] and by a single crystal *X*-ray structure analysis (see below).

Greater regioselectivity was observed in the photolysis of the diazo compound (**15d**). When methanol was used as a ketene trap, the n.m.r. spectrum of the crude photolysate was complicated by the presence of dimethyl malonate and the hydrazone (**20**), formed by a competing fragmentation reaction,[1] although the methyl ester signals of the diazetidinones (**16d**) and (**17d**) (Nu = MeO) were tentatively assigned. Chromatography failed to remove the hydrazone (**20**) and separate the isomers. However, irradiation in the presence of water gave the corresponding acids (**16d**) and (**17d**) (Nu = HO) uncontaminated with (**20**), which were decarboxylated, and the resulting C-4 unsubstituted diazetidinones (**18**) and (**19**) separated by chromatography, and the ratio of the isolated yields determined.



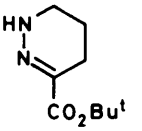
(**20**) $R^1 = CH_2Ph$, $R^2 = CO_2Et$, $R^3 = H$
(**21**) $R^1 = Me$, $R^2 = CO_2Et$, $R^3 = H$
(**22**) $R^1 = Me$, $R^2 = Ph$, $R^3 = CO_2CH_2Ph$

When the benzyl group was replaced by a methyl as in diazo compound (**15e**), the major products from photolysis in the presence of methanol were dimethyl malonate and the hydrazone (**21**). Chromatography removed the dimethyl malonate and gave an inseparable mixture of the hydrazone (**21**) and the diazetidinones (**16e**; Nu = MeO) and (**17e**; Nu = MeO). By careful inspection of the ^1H n.m.r. spectrum of this mixture it was possible to determine the ratio of (**16e**; Nu = MeO) to (**17e**; Nu = MeO) as 2:1, although it was not possible to separate the pure diazetidinones.

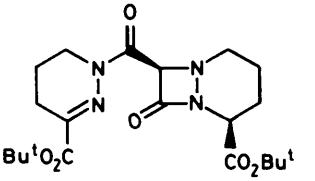
Irradiation of the diazo compound (**15f**) gave no detectable aza-β-lactams, and even the hydrazone (**22**) was not formed by the alternative fragmentation pathway. This result was particularly disappointing in that the aza-β-lactam (**16f**) would have been a useful model for the synthesis of an aza-nocardicin analogue.

The reluctance of an *N*-alkyl group bearing an electron withdrawing ester substituent to migrate, observed in the photolysis of (**15d**) and (**15e**), is more marked in the ring contraction of the bicyclic diazo compound (**15g**), where the Wolff rearrangement was highly regio- and stereo-selective and only one of the possible regioisomeric diazetidinones was isolated. However, the yields of four-membered ring products were low since fragmentation of the intermediate to carbon suboxide and the tetrahydropyridazine (**23**) (formed by isomerisation of the initially formed 3,4,5,6-tetrahydro isomer) competes very effectively with ring contraction. When the photolysis of (**15g**) was carried out in the presence of ethanol, diethyl malonate (46%) and the pyridazine (**23**) (47%) were isolated. The pyridazine (**23**) is itself sufficiently nucleophilic to intercept the ketene intermediate involved in the ring contraction, so that when (**15g**) was irradiated in *dry* ether in the absence of added nucleophiles, the only four-membered ring product was (**24**). The carboxylic acid (**16g**; Nu = HO) is decarboxylated in poor yield to give aza-β-lactam (**18d**). Presumably the additional strain associated with the 6—4 bicyclic system makes the decarboxylation less favourable.

The structure of the bicyclic aza-β-lactam (**16g**; Nu = EtO) was assigned on the basis of n.O.e. difference experiments which



(**23**)



(**24**)

showed that the proton adjacent to the t-butyl ester group was not close to 1-H, but that 1-H was close to the axial proton at C-7. The regiochemistry of the ring contraction process was further confirmed by an *X*-ray crystallographic analysis of the 1,2-diazetidinone (**24**) (see below).

In an attempt to prepare the more highly strained bicyclic aza-β-lactam (**16h**), the diazo compound (**15h**) was irradiated in ether–ethanol. However, no four-membered ring products were formed as evidenced by the lack of a high frequency carbonyl stretch in the i.r. spectrum of the crude product.

Thus the photochemical ring contraction of unsymmetrical 4-diazopyrazolidine-3,5-diones exhibits some degree of regioselectivity, the relative migratory aptitudes of nitrogen groups following the order: NPh > $NCHPh_2$ ~ NCH_2Ph ~ NMe > NCH_2CO_2Et. The Wolff rearrangement of unsymmetrical 2-diazo-1,3-dicarbonyl compounds has been investigated, and the relative migratory aptitude of hydrogen, alkyl, aryl, and heteroatom groups studied.[8] In general the results show that in $R^1COCN_2COR^2$ an electron poor R^1–CO bond favours migration of the group R^1. If this group, R^1, possesses a lone pair of electrons capable of participating in resonance with the carbonyl, then the group R^2 migrates in preference. Thus there are several examples of carbon *vs.* heteroatom migration reported,[2–8] but very few examples in which both migrating groups are heteroatoms. The limited results available indicate that nitrogen migrates in preference to oxygen, but the present work provides the first indications of the relative migratory aptitudes of differently substituted nitrogen atoms in the Wolff rearrangement.

In the series of monocyclic diazopyrazolidinediones, the results suggest that the nitrogen bearing the more electron donating substituent migrates preferentially in the Wolff rearrangement.[9] Although it seems reasonable that the *N*-alkyl group bearing an electron-withdrawing ester substituent should be more reluctant to migrate to an electron-deficient centre, the very high selectivity observed in the ring contraction of the bicyclic diazo compound (**15g**) is puzzling, since on electronic grounds a similar ratio to that observed in the photolysis of (**15d**) was expected. One possible explanation for the increased selectivity in the bicyclic series was uncovered by a single crystal *X*-ray analysis of the diazo compound (**15g**) (Figures 1 and 2).

The *X*-ray structure shows that the geometry of the two bridgehead nitrogens is different. The migrating nitrogen atom, N-9, is the more planar of the two, the sum of the angles about N being 353.6° (*cf.* 343.9° at N-4), and it is closer to the plane defined by C(1)–C(2)–C(3) than N-4 (Figure 2). Hence one possible explanation for the observed regioselectivity lies in the hybridisation of the migrating nitrogen, the more planar nitrogen migrating because its lone pair orbital is better aligned for overlap with, in the extreme, the vacant carbene p-orbital. The less planar nitrogen atom having more sp^3 character has a lone pair less well disposed for such overlap. A similar explanation pertains to the preferred migration of the *N*-phenyl substituent, since a nitrogen bearing an *N*-aryl substituent would be expected to be more planar than a nitrogen bearing an alkyl group (see also discussion of inversion barriers below).

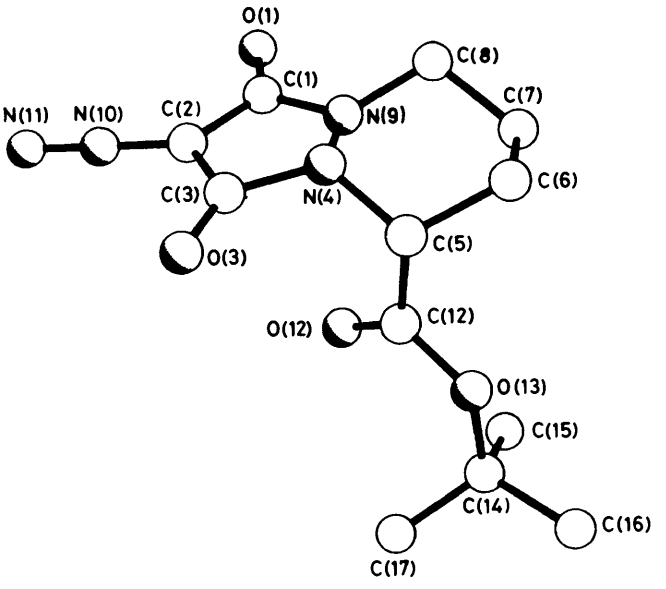


Figure 1. The molecular structure of (**15g**) giving the crystallographic numbering scheme

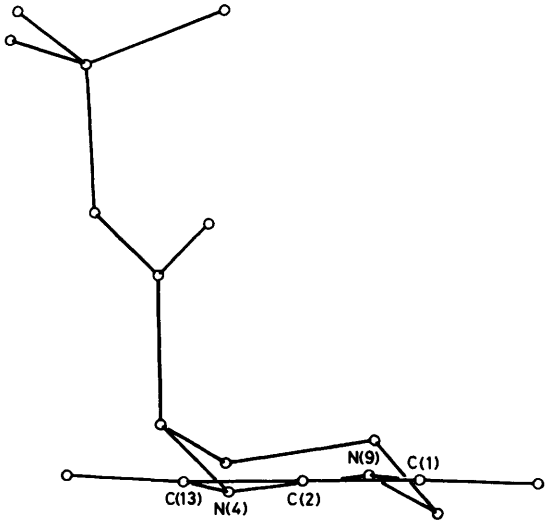


Figure 2. Edge view of the 5-membered ring of (**15g**) illustrating the relative deviations of N(4) and N(9) from the C(1),C(2),C(3) plane, and the axial disposition of the t-butyl ester. Both N(4) and N(9) are pyramidal with deviations of 0.33 and 0.20 Å respectively from the planes of their substituent atoms. N(4) Lies 0.11 Å above the C(1),C(2),C(3) plane and N(9) lies 0.05 Å below

X-*Ray Crystal Structures of* 1,2-*Diazetidinones*.—Although primarily undertaken to confirm their structures, the *X*-ray crystallographic analyses of the 1,2-diazetidinones (**17c**; Nu = EtO) (Figure 3) and (**24**) (Figures 4 and 5) are of interest in their own right, since no *X*-ray structures of 1,2-diazetidinones have been published to date.

Nitrogen Inversion in 1,2-*Diazetidinones*.—One distinctive feature of C-4 unsubstituted 1,2-diazetidinones is the magnetic non-equivalence of the C-4 hydrogens caused by the N-1 atom which is capable of pyramidal inversion. A consequence of this is that these hydrogen atoms appear as AB systems in the ^{1}H n.m.r. spectra. However, on warming the n.m.r. sample, these quartets coalesce, and hence the inversion barrier at N-1 can be determined.[10] The inversion barriers for the diazetidinones described in this work, together with known values, are shown in Table 2.

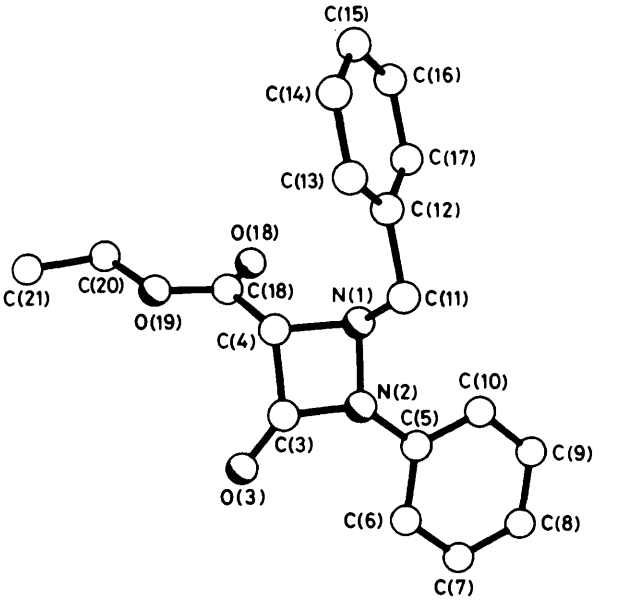


Figure 3. The molecular structure of (**17c**) giving the crystallographic numbering scheme

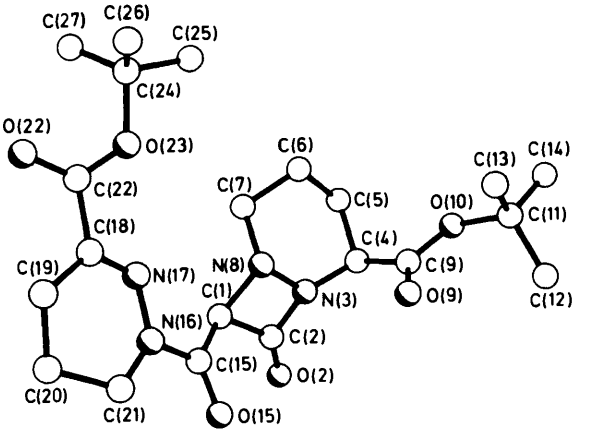


Figure 4. The molecular structure of (**24**) giving the crystallographic numbering scheme

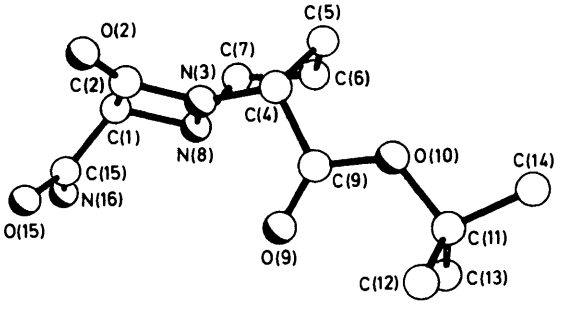


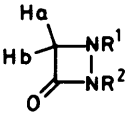
Figure 5. Partial side view of (**24**) illustrating the axial disposition of the t-butyl ester, and the respective planar and pyramidal geometries of N(3) and N(8). N(8) Lies 0.63 Å from the plane of C(1),N(3),C(7)

Table 2. N-1 Inversion barriers for 1,2-diazetidinones

Compd.	R^1	R^2	$\Delta G^{\ddagger}$ (kcal mol^{-1})
(**18a**)	Me	$CHPh_2$	19.5
(**19a**)	$CHPh_2$	Me	19.1
(**19b**)	CH_2Ph	Ph	19.7
	CH_2Ph	CH_2Ph	19.0[a]
	$CHPh_2$	H	18.6[b]
	Ph	Ph	13.3[c]

[a] Ref. 1. [b] Ref. 11. [c] Ref. 12.

The results are consistent with other diazetidinones, although the diphenyl compound is reported to have a much lower



barrier as a result of the aryl substituent which flattens the pyramidal configuration at N-1. The effect of a similar flattening of nitrogen geometry by an aryl substituent in the regioselective formation of 1,2-diazetidinones has already been discussed.

Experimental

For general points see ref. 1.

Ethyl 3-Benzylidene-2-methylcarbazate (**1a**).—A vigorously stirred mixture of ethyl 3-benzylidenecarbazate[13] (500 mg, 2.6 mmol), iodomethane (730 mg, 5.1 mmol), trimethylbenzylammonium chloride (100 mg), aqueous sodium hydroxide (40%; 2 ml) and benzene (30 ml) was heated under reflux for 9 h. After cooling, the layers were separated, and the organic layer was washed with water, dried, and evaporated to give the *title compound* (**1a**) (470 mg, 88%) as a yellow syrup (Found: C, 64.4; H, 6.9; N, 13.6. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.8; N, 13.6%); $\nu_{max.}$(neat) 1 700 and 1 605 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.35 (3 H, t), 3.37 (3 H, s), 4.35 (2 H, q), 7.35 (3 H, m), and 7.72 (3 H, m); *m/z* 206 (M^+).

Ethyl 3-Benzyl-2-methylcarbazate (**2a**).—A solution of the carbazate (**1a**) (950 mg) in ethanol (35 ml) was hydrogenated over 10% palladium-on-charcoal (50 mg) to give, after distillation, the title compound (**2a**) (820 mg, 86%), b.p. 117—121 °C at 0.3 mmHg (Kugelrohr); δ_H(90 MHz; $CDCl_3$) 1.25 (3 H, t), 2.95 (3 H, s), 3.97 (2 H, s), 4.20 (2 H, q), 4.60 (1 H, br s, D_2O exch.), and 7.35 (5 H, m); *m/z* 208 (M^+), 117, 106, and 91 (base).

Ethyl 3-Benzyl-3-ethoxycarbonylacetyl-2-methylcarbazate (**3a**).—A solution of ethoxycarbonylacetyl chloride (3.8 g, 25 mmol) in benzene (25 ml) was added dropwise to a stirred, ice-cooled solution of the carbazate (**2a**) (5.2 g, 25 mmol) and triethylamine (2.5 g, 25 mmol) in benzene (100 ml). The mixture was stirred at room temperature for 12 h, filtered, and the filtrate evaporated to give the title compound (**3a**) (6.8 g, 84%), δ_H (60 MHz; $CDCl_3$) 1.13 (3 H, t), 1.29 (3 H, t), 2.89 (3 H, s), 3.40 (2 H, AB, *J* 16 Hz); 3.80—4.40 (4 H, m), 4.70 (2 H, AB, *J* 14 Hz), and 7.25 (5 H, s).

1-Benzyl-2-methylpyrazolidine-3,5-dione (**4a**).—A mixture of the carbazate (**3a**) (6.5 g, 20 mmol) and sodium ethoxide [from sodium (0.5 g, 22 mmol)] in ethanol (110 ml) was heated under reflux for 5 h. The solvent was evaporated, and the residue dissolved in water (150 ml), and extracted with ether. The aqueous layer was acidified and extracted with dichloromethane. The CH_2Cl_2 extracts were evaporated, the residue dissolved in a mixture of acetonitrile (100 ml) and water (10 ml), and the solution heated under reflux for 5 h. Evaporation followed by crystallisation of the residue from ethanol gave the *title compound* (**4a**) (4.0 g, 97%), m.p. 104 °C (Found: C, 64.6; H, 5.9; N, 13.7. $C_{11}H_{12}N_2O_2$ requires C, 64.7; H, 5.9; N, 13.7%); $\nu_{max.}$(Nujol) 1 740 and 1 695 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.05 (3 H, s), 3.23 (2 H, s), 4.83 (2 H, s), and 7.28 (5 H, m); *m/z* 204 (M^+) and 91 (base).

Ethyl 3-Benzylidene-2-phenylcarbazate (**1c**).—A solution of butyl-lithium in hexane (1.56M; 3.2 ml, 5 mmol) was added dropwise to a stirred solution of benzaldehyde phenylhydrazone (1.0 g, 5.1 mmol) in THF (8 ml) at −78 °C. The initial deep red colour was followed by the formation of a yellow precipitate. This suspension was stirred for 15 min, quenched with ethyl chloroformate (0.8 g, 8 mmol) and then warmed to room temperature. Aqueous work-up gave, after recrystallisation from cyclohexane, the *title compound* (**1c**) (1.1 g, 80%), m.p. 98.5 °C (Found: C, 71.6; H, 6.0; N, 10.4. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.0; N, 10.4%); $\nu_{max.}$(Nujol) 1 730 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.32 (3 H, t), 4.30 (2 H, q), and 7.1—7.8 (11 H, m); *m/z* 268 (M^+).

Ethyl 3-Benzyl-2-phenylcarbazate (**2c**).—This was prepared by hydrogenation of the carbazate (**1c**) exactly as described for compound (**2a**) as a yellow oil (100%), $\nu_{max.}$(neat) 3 310, 1 700, and 1 595 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.20 (3 H, t), 4.01 (2 H, d, *J* 6 Hz; gives a singlet with D_2O), 4.20 (2 H, q), 4.99 (1 H, t, *J* 6 Hz, D_2O exch.), and 6.90—7.70 (10 H, m); *m/z* 270 (M^+).

Ethyl 3-Benzyl-3-ethoxycarbonylacetyl-2-phenylcarbazate (**3c**).—This was prepared by acylation of the carbazate (**2c**) exactly as described for compound (**3a**) as a pale yellow gum (83%), $\nu_{max.}$(neat) 1 750, 1 680, and 1 600 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.10 (3 H, t), 1.27 (3 H, t), 3.45 (2 H, AB, *J* 14 Hz), 4.17 (4 H, m), 4.40 (2 H, AB, *J* 14 Hz), and 7.05—7.60 (10 H, m).

1-Benzyl-2-phenylpyrazolidine-3,5-dione (**4c**).—This was prepared from the carbazate (**3c**) exactly as described for compound (**4a**) as a colourless solid (76%), m.p. 109.5 °C (Found: C, 72.15; H, 5.3; N, 10.6. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%); $\nu_{max.}$(Nujol) 1 735, 1 710, and 1 595 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.30 (2 H, s), 4.70 (2 H, s), and 6.8—7.5 (10 H, m); *m/z* 266 (M^+) and 91 (base).

t-Butyl 3-Diphenylmethylenecarbazate (**5a**).—A mixture of benzophenone (6.88 g, 38 mmol), t-butyl carbazate (5.0 g, 38 mmol), acetic acid (1 ml) and ethanol (100 ml) was heated under reflux for 24 h. The solvent was evaporated and the residue crystallised from ethanol to give the title compound (**5a**) (10.5 g, 94%), m.p. 128 °C, $\nu_{max.}$(Nujol) 1 740 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.50 (9 H, s), and 7.0—7.7 (11 H, m).

t-Butyl 3-Diphenylmethylene-2-methylcarbazate (**6a**).—A stirred mixture of the carbazate (**5a**) (10.0 g, 33.8 mol), iodomethane (6.0 g, 42 mmol), and potassium carbonate (10 g) in acetone (300 ml) was heated under reflux for 24 h. The mixture was filtered, and the filtrate evaporated to give the *title compound* (**6a**) (10.47 g, 100%), m.p. 78 °C (Found: C, 73.5; H, 7.2; N, 9.0. $C_{19}H_{22}N_2O_2$ requires C, 73.5; H, 7.1; N, 9.0%); $\nu_{max.}$(Nujol) 1 680 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.24 (9 H, s), 3.03 (3 H, s), and 7.15—7.70 (10 H, m); *m/z* 310 (M^+), 254, 237, 209 (base), 194, 180, 165, 139, 106, 104, 91, and 77.

t-Butyl 3-Diphenylmethyl-2-methylcarbazate (**7a**).—Bromocresol Green indicator (5 mg) was added to a stirred mixture of the carbazate (**6a**) (7.87 g, 25.4 mmol) and sodium cyanoborohydride (1.76 g, 26.2 mmol) in THF (60 ml) and methanol

(5 ml) to give a dark blue solution. Dilute hydrochloric acid was then added at such a rate as to maintain a yellow colour of the solution. When the yellow colour persisted for 1 h without further addition of acid, the mixture was evaporated, and the residue partitioned between water and dichloromethane. The organic layer was separated, dried, and evaporated to give, after chromatography, the *title compound* (**7a**) (7.20 g, 91%), m.p. 68 °C (Found: C, 73.25; H, 7.8; N, 9.0. $C_{19}H_{24}N_2O_2$ requires C, 73.05; H, 7.7; N, 9.0%); $\nu_{max.}$(Nujol) 3 275 and 1 693 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.49 (9 H, s), 2.76 (3 H, s), 4.82 (1 H, br s, D_2O exch.), 5.28 (1 H, s), and 7.40 (10 H, m); *m/z* 312 (M^+), 256, 239, 167 (base), 165, 152, 104, 77, and 57.

t-Butyl 3-Diphenylmethyl-3-ethoxycarbonylacetyl-2-methylcarbazate (**8a**).—The carbazate (**7a**) (5.62 g, 18 mmol) was acylated with ethoxycarbonylacetyl chloride as described for compound (**3a**) to give the *title compound* (**8a**) (4.12 g, 54%), m.p. 72—73 °C (Found: C, 67.5; H, 7.1; N, 6.7. $C_{24}H_{30}N_2O_5$ requires C, 67.6; H, 7.1; N, 6.6%); $\nu_{max.}$(Nujol) 1 730, 1 710, and 1 677 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.28 (9 H, s), 1.35 (3 H, t), 2.98 (3 H, br s), 3.44 (2 H, AB, *J* 15 Hz), 4.22 (2 H, q), 6.65 and 6.75 (1 H, 2 br s), and 7.28 (10 H, m); *m/z* 426 (M^+) 354, 297, 167 (base), 152, 115, and 57.

1-Diphenylmethyl-2-methylpyrazolidine-3,5-dione (**4b**).—Trifluoroacetic acid (10 ml) was added to a stirred solution of the carbazate (**8a**) (4.0 g, 9.4 mmol) in dichloromethane (70 ml), and the resulting solution was stirred at room temperature for 48 h. Evaporation of the solvent, and chromatography gave the *title compound* (**4b**) (2.30 g, 87%), m.p. 107.5 °C (Found: C, 72.7; H, 5.7; N, 9.9. $C_{17}H_{16}N_2O_2$ requires C, 72.8; H, 5.75; N, 10.0%); $\nu_{max.}$(Nujol) 1 730 and 1 685 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 2.95 (3 H, s), 3.13 (2 H, s), 6.74 (1 H, s), and 7.30 (10 H, s); *m/z* 280 (M^+), 167 (base), and 152.

t-Butyl 3-Benzylidenecarbazate (**5b**).—This was prepared by the literature method, [14] m.p. 184—188 °C (lit., 185—187 °C).

t-Butyl 3-Benzylidene-2-(ethoxycarbonylmethyl)carbazate (**6b**).—Alkylation of the carbazate (**5b**) (5.0 g, 23 mmol) with ethyl bromoacetate (4.2 g, 27 mmol) under the conditions described for compound (**6a**) gave the *title compound* (**6b**) (5.15 g, 74%), m.p. 79 °C (from ethyl acetate–light petroleum) (Found: C, 62.9; H, 7.3; N, 9.1. $C_{16}H_{22}N_2O_4$ requires C, 62.7; H, 7.2; N, 9.1%); $\nu_{max.}$(Nujol) 1 743, 1 695, and 1 610 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.20 (3 H, t), 1.53 (9 H, s), 4.11 (2 H, q), 4.50 (2 H, s), 7.21 (3 H, m), 7.54 (2 H, m), and 7.85 (1 H, s); *m/z* 306 (M^+), 206, 133, 88 (base), and 57.

t-Butyl 3-Benzyl-2-(ethoxycarbonylmethyl)carbazate (**7b**).—A solution of the carbazate (**6b**) (4.0 g) in ethanol (100 ml) was hydrogenated over 10% palladium–charcoal (0.3 g). The catalyst was filtered off, and the filtrate evaporated to give the title compound (**7b**) (3.83 g, 95%) as a pale yellow oil, $\nu_{max.}$(neat) 3 300, 1 745, and 1 705 cm^{-1}; δ_H (60 MHz, $CDCl_3$) 1.25 (3 H, t), 1.50 (9 H, s), 3.90 (2 H, br, sharpens with D_2O), 3.95 (2 H, s), 4.05 (2 H, q), 4.4 (1 H, br s, D_2O exch.), and 7.15 (5 H, s); *m/z* 308 (M^+), 266, 235, 208 (base), 135, 91, 57.

t-Butyl 3-Benzyl-3-ethoxycarbonylacetyl-2-(ethoxycarbonylmethyl)carbazate (**8b**).—Acylation of the carbazate (**7b**) (3.97 g, 12.9 mmol) with ethoxycarbonylacetyl chloride under the conditions described for compound (**3a**) gave the title compound (**8b**) (2.9 g, 53%) as a colourless gum, $\nu_{max.}$(neat) 1 740, 1 720, and 1 680 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.18 (3 H, t), 1.32 (3 H, t), 1.43 (9 H, s), 3.65 (2 H, AB, *J* 16 Hz), 3.90 (4 H, m), 4.20 (2 H, q), and 7.3 (5 H, s).

1-Benzyl-2-(ethoxycarbonylmethyl)pyrazolidine-3,5-dione (**4d**).—The carbazate (**8b**) (0.6 g, 1.4 mmol) was treated with TFA under the conditions described for compound (**4b**) to give the *title compound* (**4d**) (0.36 g, 92%), m.p. 83 °C (Found: C, 60.95; H, 5.85; N, 10.2. $C_{14}H_{16}N_2O_4$ requires C, 60.9; H, 5.8; N, 10.1%); $\nu_{max.}$(Nujol) 1 755 and 1 695 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.17 (3 H, t), 3.34 (2 H, s), 4.05 (2 H, q), 4.17 (2 H, s), 4.79 (2 H, s), and 7.30 (5 H, m); *m/z* 276 (M^+), 203 and 91 (base).

t-Butyl 3-Ethoxycarbonylmethyl-2-methylcarbazate (**7c**).—A solution of benzyl chloroformate (4.7 g, 27 mmol) in benzene (30 ml) was added dropwise to a stirred ice-cooled solution of t-butyl 3-(ethoxycarbonylmethyl)carbazate [5] (6.0 g, 27 mmol) and triethylamine (2.79 g, 27 mmol) in benzene (100 ml). The resulting suspension was stirred at room temperature for 12 h, and then filtered. The filtrate was evaporated under reduced pressure and the residue crystallised from ethanol to give *t-butyl 3-benzyloxycarbonyl-3-(ethoxycarbonylmethyl)carbazate* (7.0 g, 74%), m.p. 120 °C (Found: C, 57.9; H, 7.0; N, 7.9. $C_{17}H_{24}N_2O_6$ requires C, 57.9; H, 6.9; N, 7.95%); $\nu_{max.}$(Nujol) 3 325, 1 747, and 1 705 cm^{-1}.

A stirred mixture of the above compound (5.0 g, 14 mmol), iodomethane (2.12 g, 15 mmol), and potassium carbonate (7.8 g) in acetone was heated under reflux for 24 h. The mixture was filtered and the filtrate evaporated to give t-butyl 3-benzyloxycarbonyl-3-ethoxycarbonylmethyl-2-methylcarbazate (4.8 g, 92%) as a colourless oil.

Without further purification, the above oil (2.76 g) was dissolved in ethanol (70 ml) and hydrogenated over 10% palladium–charcoal (0.08 g). The catalyst was filtered off, the filtrate evaporated, and the residue distilled to give the *title compound* (**7c**) (1.73 g, 99%), b.p. 95—100 °C at 0.2 mmHg (Kugelrohr) (Found: C, 51.6; H, 8.6; N, 11.8. $C_{20}H_{20}N_2O_4$ requires C, 51.7; H, 8.7; N, 12.1%); $\nu_{max.}$(neat) 3 320, 1 743, and 1 695 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.25 (3 H, t), 1.44 (9 H, s), 3.03 (3 H, s), 3.61 (2 H, s), 4.17 (2 H, q), and 4.90 (1 H, br s); *m/z* 232 (M^+), 176, 132, 103, 85, 76, 59, and 57 (base).

t-Butyl 3-Ethoxycarbonylacetyl-3-ethoxycarbonylmethyl-2-methylcarbazate (**8c**).—Acylation of the carbazate (**7c**) (3.5 g, 15.1 mmol) with ethoxycarbonylacetyl chloride under the conditions described for compound (**3a**) gave the title compound (**8c**) (4.07 g, 78%) as a colourless oil, $\nu_{max.}$(neat) 1 745, 1 720, and 1 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.30 (6 H, t), 1.49 (9 H, s), 3.21 (3 H, s), 3.42 (2 H, AB, *J* 13 Hz), 4.17 (2 H, AB, *J* 17 Hz), and 4.22 (4 H, q); *m/z* 346 (M^+).

1-Ethoxycarbonylmethyl-2-methylpyrazolidine-3,5-dione (**4e**).—The carbazate (**8c**) (3.95 g, 11.4 mmol) was treated with TFA under the conditions described for compound (**4b**) to give the *title compound* (**4e**) (1.45 g, 63%), m.p. 95.5 °C (Found: C, 47.8; H, 6.0; N, 14.0. $C_8H_{12}N_2O_4$ requires C, 48.0; H, 6.0; N, 14.0%); $\nu_{max.}$(Nujol) 1 740 and 1 695 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.38 (3 H, t), 3.12 (3 H, s), 3.24 (2 H, s), 4.23 (2 H, q), and 4.37 (2 H, s); *m/z* 200 (M^+), 127 (base), 99, and 85.

t-Butyl 3-(Benzyloxycarbonyl)benzylidenecarbazate (**5d**).—A mixture of benzyl benzoylformate (1.0 g, 4.1 mmol), t-butylcarbazate (0.55 g, 4.1 mmol) and acetic acid (0.3 ml) was heated under reflux for 3 h in ethanol (40 ml). The solvent was evaporated and the residue crystallised from a mixture of light petroleum (30 ml) and ethanol (5 ml) to give the *title compound* (**5d**) (1.20 g, 81%), m.p. 131 °C (Found: C, 67.7; H, 6.2; N, 7.9. $C_{20}H_{22}N_2O_4$ requires C, 67.8; H, 6.3; N, 7.9%); $\nu_{max.}$(Nujol) 3 340, 1 713, and 1 750 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.48 (9 H, s), 5.17 (2 H, s), 6.98—7.70 (10 H, m), and 11.33 (1 H, br s); *m/z* 354 (M^+).

t-Butyl 3-(*Benzyloxycarbonyl*)*benzylidene*-2-*methylcarbazate* (**6d**).—Alkylation of the carbazate (**5d**) (4.3 g, 12 mmol) with iodomethane under the conditions described for compound (**6a**) gave the title compound (**6d**) (4.25 g, 95%) as a yellow oil, $\nu_{max.}$(neat) 1 735 and 1 705 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.44 (9 H, s), 3.20 (3 H, s), 5.21 (2 H, s), 7.32 (8 H, m), and 7.68 (2 H, m); *m/z* 368 (M^+).

t-Butyl 3-(*Benzyloxycarbonyl*)*benzyl*-2-*methylcarbazate* (**7d**).—Reduction of the carbazate (**6d**) (2.25 g) with sodium cyanoborohydride under the conditions described for compound (**7a**) gave the *title compound* (**7d**) (1.28 g, 57%) as a colourless oil (Found: C, 68.4; H, 7.3; N, 7.6. $C_{21}H_{26}N_2O_4$ requires C, 68.1; H, 7.1; N, 7.6%); $\nu_{max.}$(neat) 3 300, 1 745, and 1 695 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.49 (9 H, s), 3.40 (3 H, s), 4.86 (1 H, br s, D_2O exch.), 4.93 (1 H, br s, sharpens with D_2O), 5.15 (2 H, s), and 7.30 (10 H, m); *m/z* 370 (M^+) and 91 (base).

t-Butyl 3-(*Benzyloxycarbonyl*)*benzyl*-3-*ethoxycarbonylacetyl*-2-*methylcarbazate* (**8d**).—Acylation of the carbazate (**7d**) (1.3 g, 3.5 mmol) with ethoxycarbonylacetyl chloride under the conditions described for compound (**3a**) gave the title compound (**8d**) (0.85 g, 50%) as a colourless gum, $\nu_{max.}$(neat) 1 740, 1 715, and 1 690 cm^{-1}; used without further purification.

1-(*Benzyloxycarbonyl*)*benzyl*-2-*methylpyrazolidine*-3,5-*dione* (**4f**).—The carbazate (**8d**) (0.85 g) was treated with TFA under the conditions described for compound (**4b**) to give the *title compound* (**4f**) (0.55 g, 93%) as a pale yellow gum (Found: C, 67.2; H, 5.2; N, 8.15. $C_{19}H_{18}N_2O_4$ requires C, 67.45; H, 5.4; N, 8.3%); $\nu_{max.}$(neat) 1 745 and 1 710 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.92 (3 H, s), 3.19 (2 H, s), 5.29 (2 H, s), 6.22 (1 H, s), and 7.32 (10 H, m); *m/z 338* (M^+), 203, 167, and 91 (base).

t-Butyl 1-*Benzyloxycarbonylpyrazolidine*-3-*carboxylate* (**12**).—A solution of diazomethane in ether was added to freshly distilled t-butyl acrylate (17.5 g, 0.136 mol) until a yellow colour persisted for 2 min. The ether was evaporated and the residue was immediately dissolved in ethanol (300 ml) and hydrogenated over 10% palladium-on-charcoal. The catalyst was filtered off, the filtrate evaporated, and the residue redissolved in ethyl acetate (260 ml). This solution was added to a solution of sodium hydrogen carbonate (24 g) in water (260 ml), and then the vigorously stirred ice-cooled mixture was treated with a solution of benzyl chloroformate (18.76 g, 0.11 mol) in ethyl acetate (50 ml). After 2 h, the organic layer was separated, washed with dilute hydrochloric acid and water, dried, and evaporated. Chromatography of the residue gave (i) t-butyl 4,5-dihydropyrazole-3-carboxylate (**9**) (9 g, 39%), $\nu_{max.}$(neat) 3 300 and 1 690 cm^{-1}; and (ii) the title compound (**12**) (7.35 g, 18% overall); $\nu_{max.}$(neat) 3 250, 1 725, and 1 700 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.50 (9 H, s), 1.80—2.50 (2 H, m), 3.40—4.00 (2 H, m), 4.50 (2 H, m), 5.23 (2 H, s), and 7.35 (5 H, s).

t-Butyl 1-*Benzyloxycarbonyl*-2-(*ethoxycarbonylacetyl*)*pyrazolidine*-3-*carboxylate* (**13**).—Acylation of the pyrazolidine (**12**) (2.5 g, 8.1 mmol) with ethoxycarbonylacetyl chloride under the conditions described for compound (**3a**) gave the *title compound* (**13**) (2.9 g, 84%), m.p. 68 °C (Found: C, 59.9; H, 6.7; N, 6.6. $C_{21}H_{28}N_2O_7$ requires C, 60.0; H, 6.7; N, 6.7%); $\nu_{max.}$(Nujol) 1 730 and 1 690 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.22 (3 H, t), 1.41 (9 H, s), 2.23 (1 H, m), 2.37 (1 H, m), 3.20 (1 H, m), 3.49 (2 H, AB, *J* 15 Hz), 4.11 (3 H, m), 4.92 (1 H, dd, *J* 7.5, 4.5 Hz), 5.22 (2 H, AB, *J* 12 Hz), and 7.35 (5 H, m); *m/z* 420 (M^+).

t-Butyl 2-(*Ethoxycarbonylacetyl*)*pyrazolidine*-3-*carboxylate* (**14**).—A solution of the pyrazolidine (**13**) (4.6 g) in ethanol (100 ml) was hydrogenated over 10% palladium-on-charcoal (0.5 g). The catalyst was filtered off and the filtrate evaporated to give the *title compound* (**14**) (3.1 g, 99%), m.p. 65 °C (Found: C, 54.6; H, 7.8; N, 9.8. $C_{13}H_{22}N_2O_5$ requires C, 54.5; H, 7.7; N, 9.8%); $\nu_{max.}$(Nujol) 3 250, 1 735, and 1 650 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.27 (3 H, t), 1.46 (9 H, s), 2.02 (1 H, m), 2.54 (1 H, m), 2.86 (1 H, m), 3.19 (1 H, m), 3.59 (2 H, AB, *J* 14 Hz), 3.62 (1 H, m), 4.18 (2 H q), and 4.40 (1 H, dd, *J* 9, 7 Hz); *m/z* 286 (M^+).

t-Butyl 1,3-*Dioxo*-1H-*pyrazolo*[1,2-a]*pyrazolidine*-5-*carboxylate* (**4h**).—A mixture of the pyrazolidine (**14**) (480 mg) and sodium ethoxide [from sodium hydride (44 mg)] in ethanol (20 ml) was heated under reflux for 8 h. The solvent was evaporated, and the residue partitioned between ether and water. The aqueous layer was separated, acidified, and extracted with dichloromethane. The CH_2Cl_2 extracts were dried, evaporated, and the residue crystallised from hexane–ethyl acetate to give the *title compound* (**4h**) (230 mg, 57%), m.p. 108 °C (Found: C, 54.8; H, 6.7; N, 11.5. $C_{11}H_{16}N_2O_4$ requires C, 55.0; H, 6.7; N, 11.7%); $\nu_{max.}$(Nujol) 1 735, 1 705, and 1 690 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.49 (9 H, s), 2.46—2.78 (2 H, m), 3.39 (2 H, AB, *J* 20 Hz), 3.55 (1 H, m), 3.93 (1 H, m), and 4.61 (1 H, dd, *J* 6, 1 Hz); *m/z* 240 (M^+), 184, 139 (base), 97, 85, 83, and 57.

4-*Diazopyrazolidine*-3,5-*diones* (**15**): *General Procedure*.—Triethylamine (1 mol equiv.) was added dropwise to a stirred ice-cooled solution of the pyrazolidine-3,5-dione (**4**) (1 mol equiv.) and toluene-*p*-sulphonyl azide (2 mol equiv.) in dichloromethane [or acetonitrile for compounds (**4c**) and (**4h**)]. The mixture was stirred at room temperature until t.l.c. indicated that no more pyrazolidinedione remained; the product diazo compounds are usually less polar, and show up very strongly under u.v. light. The reaction mixture was evaporated, and the residue triturated with ether. The insoluble toluene-*p*-sulphonamide was filtered off and the ether washed with aqueous sodium hydroxide (5%) and water, dried, and evaporated. The residue was purified by chromatography to give unchanged toluene-*p*-sulphonyl azide, followed by the diazo compound (**15**). The following compounds were prepared:

1-*Benzyl*-4-*diazo*-2-*methylpyrazolidine*-3,5-*dione* (**15a**) (42%), m.p. 58.5 °C (Found C, 57.6; H, 4.35; N, 24.4. $C_{11}H_{10}N_4O_2$ requires C, 57.4; H, 4.4; N, 24.3%); $\nu_{max.}$(Nujol) 2 150, 1 730, and 1 690 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 3.03 (3 H, s), 4.75 (2 H, s), and 7.23 (5 H, m); *m/z* 230 (M^+), 204, and 91 (base).

4-*Diazo*-1-*diphenylmethyl*-2-*methylpyrazolidine*-3,5-*dione* (**15b**) (63%), m.p. 104.5 °C (Found: C, 66.75; H, 4.6; N, 18.4. $C_{17}H_{14}N_4O_2$ requires C, 66.7; H, 4.6; N, 18.3%); $\nu_{max.}$(Nujol) 2 140 and 1 690 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 2.90 (3 H, s), 6.6 (1 H, s), and 7.30 (10 H, m); *m/z* 306 (M^+), 167 (base), 152, 139, 115, and 91.

1-*Benzyl*-4-*diazo*-2-*phenylpyrazolidine*-3,5-*dione* (**15c**) (60%), m.p. 136.5 °C (Found: C, 65.6; H, 4.1; N, 19.25. $C_{16}H_{12}N_4O_2$ requires C, 65.75; H, 4.1; N, 19.1%); $\nu_{max.}$(Nujol) 2 150, 1 708, and 1 685 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 4.70 (2 H, s) and 6.95—7.67 (10 H, m); *m/z* 292 (M^+), 266, and 91 (base).

Ethyl (2-*benzyl*-4-*diazo*-3,5-*dioxopyrazolidin*-1-*yl*)*acetate* (**15d**) (51%), m.p. 86 °C (Found: C, 55.7; H, 4.6; N, 18.5. $C_{14}H_{14}N_4O_4$ requires C, 55.6; H, 4.7; N, 18.5%); $\nu_{max.}$(Nujol) 2 150, 1 745, and 1 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.18 (3 H, t), 4.08 (2 H, q), 4.17 (2 H, s), 4.73 (2 H, s), and 7.25 (5 H, m); *m/z* 302 (M^+), 200, 155, and 91 (base).

Ethyl (4-*diazo*-3,5-*dioxo*-2-*methylpyrazolidin*-1-*yl*)*acetate* (**15e**) (71%), m.p. 63 °C (Found: C, 42.35; H, 4.4; N, 24.6. $C_8H_{10}N_4O_4$ requires C, 42.5; H, 4.7; N, 24.8%); $\nu_{max.}$(Nujol) 2 140, 1 745, 1 720, and 1 680 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.30 (3 H, t), 3.12 (3 H, s), 4.23 (2 H, q), and 4.33 (2 H, s); *m/z* 226 (M^+), 153, 127, 68, and 43.

Benzyl (4-*diazo* -3,5-*dioxo*-2-*methylpyrazolidin*-1-*yl*)(*phenyl*)-

acetate (**15f**) (49%), m.p. 165.5 °C (Found: C, 62.5; H, 4.4; N, 15.2. $C_{19}H_{16}N_4O_4$ requires C, 62.6; H, 4.4; N, 15.4%); $\nu_{max.}$(Nujol) 2 140, 1 740, and 1 687 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.72 (3 H, s), 5.34 (2 H, s), 6.22 (1 H, br s), and 7.30 (10 H, m); *m/z* 229 (base, $M^+ - CO_2CH_2Ph$).

t-Butyl 2-diazo-1,3-dioxo-hexahydro-1H-pyrazolo[1,2-a]-pyridazine-5-carboxylate (**15g**) (68%), m.p. 138 °C (Found: C, 51.2; H, 5.8; N, 19.8. $C_{12}H_{16}N_4O_4$ requires C, 51.4; H, 5.75; N, 20.0%); $\nu_{max.}$(Nujol) 2 120, 1 730, 1 713, and 1 690 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.46 (9 H, s), 1.50—1.95 (3 H, m), 2.32 (1 H, m), 3.01 (1 H, dt, *J* 13, 3 Hz), 4.14 (1 H, m), and 4.73 (1 H, m); *m/z* 280 (M^+), 224, 179 (base), 151, 83, 55, and 41.

t-Butyl 2-diazo-1,3-dioxo-1H-pyrazolo[1,2-a]pyrazolidine-5-carboxylate (**15h**) (63%), m.p. 107 °C (Found: C, 49.6; H, 5.2; N, 21.0. $C_{11}H_{14}N_4O_4$ requires C, 49.6; H, 5.3; N, 21.0%); $\nu_{max.}$(Nujol) 2 130, 1 740, and 1 670 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.48 (9 H, s), 2.47—2.59 (1 H, m), 2.67 (1 H, m), 3.57 (1 H, dt, *J* 11.7 Hz); 3.85 (1 H, m), and 4.56 (1 H, dd, *J* 11.7 Hz); *m/z* 266 (M^+), 210, 165, 87, and 57 (base).

Photolysis of the Diazo Compound (**15a**).—(a) *In ether and ethanol.* A solution of the diazo compound (**15a**) (731 mg) in dry ether (300 ml) and ethanol (20 ml) was irradiated for 4.5 h. Evaporation of the solvents and chromatography of the residue gave (i) diethyl malonate (130 mg, 26%) and (ii) a mixture of the diazetidinones (**16a**; Nu = EtO) and (**17a**; Nu = EtO) (234 mg, 30%) in the ratio 1:1 by n.m.r. This mixture was re-chromatographed to give (i) *ethyl 2-benzyl-1-methyl-3-oxo-1,2-diazetidine-4-carboxylate* (**16a**; Nu = EtO) (78 mg) as a colourless oil, $\nu_{max.}$(neat) 1 783 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.30 (3 H, t), 2.58 (3 H, s), 4.28 (2 H, qq), 4.37 (1 H, s), 4.59 (2 H, AB, *J* 15.7 Hz), and 7.35 (5 H, m); *m/z* 249 (M^+ + H), 175, 147, 133, 106, 91 (base), 77, 65, and 42; (ii) a mixture of the diazetidinones (**16a**; Nu = EtO) and (**17a**; Nu = EtO) (89 mg); and (iii) *ethyl 1-benzyl-2-methyl-3-oxo-1,2-diazetidine-4-carboxylate* (**17a**; Nu = EtO) (67 mg) as a yellow gum (Found: M^+ 248.1158. $C_{13}H_{16}N_2O_3$ requires 248.1160); $\nu_{max.}$(neat) 1 785 and 1 747 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.25 (3 H, t), 2.92 (3 H, d, *J* 0.65 Hz), 4.01 (2 H, AB, *J* 12.5 Hz), 4.20 (2 H, q), 4.47 (1 H, d, *J* 0.65 Hz), and 7.40 (5 H, m); *m/z* 248 (M^+), 234, 192, 174, 147, 117, 91 (base), 65, and 43.

(b) *In wet ether.* A solution of the diazo compound (**15a**) (312 mg) in wet ether (200 ml) was irradiated for 3.25 h. The mixture was extracted with aqueous potassium hydrogen carbonate and the aqueous layer then acidified, and extracted with dichloromethane. The CH_2Cl_2 extracts were dried and evaporated to give a mixture of 2-benzyl-1-methyl-3-oxo-1,2-diazetidine-4-carboxylic acid (**16a**; Nu = HO) and 1-benzyl-2-methyl-3-oxo-1,2-diazetidine-4-carboxylic acid (**17a**; Nu = HO) (97 mg, 33%) in the ratio 1:1 by n.m.r.; $\nu_{max.}$(neat) 3 500—2 400, 1 783, and 1 745 cm^{-1}; δ_H (90 MHz; $CDCl_3$) for (**16a**; Nu = HO) 2.59 (3 H, s), 4.52 (3 H, m), 7.28 (5 H, m), and 9.26 (1 H, br s); for (**17a**; Nu = HO) 2.88 (3 H, s), 4.02 (2 H, AB, *J* 13 Hz), 4.42 (1 H, s), 7.28 (5 H, m), and 9.26 (1 H, br s).

Photolysis of the Diazo Compound (**15b**).—(a) *In ether and ethanol.* A solution of the diazo compound (**15b**) (634 mg) in dry ether (300 ml) and ethanol (20 ml) was irradiated for 4.5 h. The solvent was evaporated and the residue chromatographed to give (i) diethyl malonate (99 mg, 30%) and (ii) a mixture of the diazetidinones (**16b**; Nu = EtO) and (**17b**; Nu = EtO) (246 mg, 36%) in the ratio 1:1 by n.m.r. This mixture was re-chromatographed to give (i) *ethyl 1-diphenylmethyl-2-methyl-3-oxo-1,2-diazetidine-4-carboxylate* (**17b**; Nu = EtO) (40 mg) as a colourless oil, $\nu_{max.}$(neat) 1 785 and 1 742 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.22 (3 H, t), 2.53 (3 H, d, *J* 0.65 Hz), 4.13 (2 H, qq), 4.42 (1 H, d, *J* 0.65 Hz), 4.68 (1 H, s), 7.18—7.42 (6 H, m), and 7.45—7.60 (4 H, m); *m/z* 324 (M^+), 266, 251, 247, 238, 223, 192, 167 (base), 152, and 91; (ii) a mixture of diazetidinones (**16b**; Nu = EtO) and (**17b**; Nu = EtO) (170 mg); and (iii) *ethyl 2-diphenylmethyl-1-methyl-3-oxo-1,2-diazetidine-4-carboxylate* (**16b**; Nu = EtO) (32 mg) as a colourless oil (Found: M^+ 324.1477. $C_{19}H_{20}N_2O_3$ requires 324.1472); $\nu_{max.}$(neat) 1 783 and 1 742 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.28 (3 H, t), 2.51 (3 H, s), 4.26 (2 H, q), 4.32 (1 H, s), 5.93 (1 H, s), and 7.15—7.52 (10 H, m); *m/z* 324 (M^+), 167 (base), 165, 152, and 77.

(b) *In wet ether.* A solution of the diazo compound (**15b**) (534 mg) in wet ether (300 ml) was irradiated for 4.5 h. Extractive work-up as described above gave a mixture of 2-diphenylmethyl-1-methyl-3-oxo-1,2-diazetidine-4-carboxylic acid (**16b**; Nu = HO) and 1-diphenylmethyl-2-methyl-3-oxo-1,2-diazetidine-4-carboxylic acid (**17b**; Nu = HO) (168 mg, 33%) in the ratio 1:1 by n.m.r., $\nu_{max.}$(neat) 3 600—2 500, 1 765, and 1 720 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 2.50 (s), 4.37 (s), 4.70 (d), 5.90 (s), 7.1—7.6 (m), and 8.5 (br s).

This mixture of carboxylic acids (98 mg) was dissolved in benzene (20 ml) and heated under reflux for 4 h. Evaporation of the solvent and chromatography of the residue gave a mixture of the diazetidinones (**18a**) and (**19a**) (80 mg, 95%) in the ratio 1:1 by n.m.r. This mixture was rechromatographed to give (i) *1-diphenylmethyl-2-methyl-1,2-diazetidin-3-one* (**19a**) (39 mg), m.p. 135 °C (Found: C, 76.3; H, 6.2; N, 10.8. $C_{17}H_{16}N_2O$ requires C, 76.2; H, 6.4; N, 11.1%); $\nu_{max.}$(Nujol) 1 765 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.46 (3 H, d, *J* 0.8 Hz), 3.72 (1 H, dd, *J* 13.5, 0.8 Hz), 4.32 (1 H, d, *J* 13.5 Hz), 4.57 (1 H, s), 7.17—7.38 (6 H, m), and 7.40—7.52 (4 H, m); *m/z* 252 (M^+), 209, 182, 167 (base), 152, 132, 104, 85, 77, and 43; (ii) *2-diphenylmethyl-1-methyl-1,2-diazetidin-3-one* (**18a**) (37 mg) (Found: C, 76.0; H, 6.4; N, 11.1%); $\nu_{max.}$(Nujol) 1 768 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.46 (3 H, s), 4.06 (2 H, AB, *J* 13.6 Hz), 5.91 (1 H, s), and 7.20—7.50 (10 H, m); *m/z* 252 (M^+), 167 (base), 166, 152, and 91.

Photolysis of the Diazo Compound (**15c**).—(a) *In ether and ethanol.* A solution of the diazo compound (**15c**) (740 mg) in dry ether (300 ml) and ethanol (25 ml) was irradiated for 3.3 h. Evaporation of the solvents and chromatography of the residue gave a mixture of the diazetidinones (**16c**; Nu = EtO) and (**17c**; Nu = EtO) (580 mg, 72%) in the ratio 1.7:1 by n.m.r. This mixture was re-chromatographed to give (i) *ethyl 1-benzyl-3-oxo-2-phenyl-1,2-diazetidine-4-carboxylate* (**17c**; Nu = EtO) (26 mg) as colourless *needles*, m.p. 71.5 °C (Found: C, 70.0; H, 5.75; N, 9.0. $C_{18}H_{18}N_2O_3$ requires C, 69.7; H, 5.85; N, 9.0%); $\nu_{max.}$(Nujol) 1 780 and 1 758 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.19 (3 H, t), 4.16 (2 H, q), 4.20 (2 H, AB, *J* 13 Hz), 4.54 (1 H, s), and 6.90—7.36 (10 H, m); *m/z* 310 (M^+) and 91 (base); (ii) a mixture of diazetidinones (361 mg); and (iii) *ethyl 2-benzyl-3-oxo-1-phenyl-1,2-diazetidine-4-carboxylate* (**16c**; Nu = HO) (163 mg), $\nu_{max.}$(neat) 1 785 and 1 750 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.28 (3 H, t), 4.26 (2 H, q), 4.67 (2 H, AB, *J* 16 Hz), 4.82 (1 H, s), 6.90—7.10 (2 H, m), and 7.13—7.47 (10 H, m); *m/z* 310 (M^+), 205, 104 (base), 91, and 77.

(b) *In wet ether.* A solution of the diazo compound (**15c**) (740 mg) in wet ether (300 ml) was irradiated for 4 h. Extractive work-up gave a mixture of 2-benzyl-3-oxo-1-phenyl-1,2-diazetidine-4-carboxylic acid (**16c**; Nu = HO) and 1-benzyl-3-oxo-2-phenyl-1,2-diazetidine-4-carboxylic acid (**17c**; Nu = HO) (397 mg, 55%) in the ratio 1.6:1 by n.m.r., $\nu_{max.}$(neat) 3 600—2 400 and 1 780—1 730br cm^{-1}; δ_H (250 MHz; $CDCl_3$) for (**16c**; Nu = HO) 4.59 (2 H, AB, *J* 15 Hz), 4.76 (1 H, s), 6.93—7.40 (m), and 9.55 (br s); for (**17c**; Nu = HO) 4.15 (2 H, AB, *J* 13 Hz), 4.65 (1 H, s), 6.93—7.40 (m), and 9.55 (br s).

The mixture of carboxylic acids (230 mg) was dissolved in benzene (30 ml) and heated under reflux for 2 h. Evaporation of the solvent and chromatography of the residue gave an inseparable mixture of 2-benzyl-1-phenyl-1,2-diazetidin-3-one (**18b**) and 1-benzyl-2-phenyl-1,2-diazetidin-3-one (**19b**) (185 mg,

Table 3. Atom co-ordinates (× 10^4) for (**15g**)

Atom	*x*	*y*	*z*
C(1)	6 051(5)	3 814(1)	2 572(2)
O(1)	7 602(4)	4 124(1)	3 127(2)
C(2)	5 496(5)	3 809(1)	1 451(2)
C(3)	3 424(5)	3 391(1)	1 144(2)
O(3)	2 503(4)	3 232(1)	277(2)
N(4)	2 630(4)	3 189(1)	2 076(2)
C(5)	1 631(4)	2 524(1)	2 197(2)
C(6)	721(5)	2 463(1)	3 273(2)
C(7)	2 670(5)	2 659(1)	4 133(2)
C(8)	3 610(5)	3 357(1)	3 945(2)
N(9)	4 394(4)	3 385(1)	2 905(2)
N(10)	6 737(6)	4 125(1)	800(2)
N(11)	7 791(8)	4 403(2)	238(3)
C(12)	3 536(4)	2 004(1)	1 988(2)
O(12)	5 570(3)	2 139(1)	1 776(2)
O(13)	2 646(3)	1 396(1)	2 079(2)
C(14)	4 197(5)	793(1)	1 991(2)
C(15)	6 257(6)	805(2)	2 849(3)
C(16)	2 469(7)	237(2)	2 172(4)
C(17)	5 159(8)	763(2)	938(3)

Table 4. Bond lengths (Å) for (**15g**)

C(1)–O(1)	1.224(3)	C(1)–C(2)	1.440(4)
C(1)–N(9)	1.353(3)	C(2)–C(3)	1.437(4)
C(2)–N(10)	1.296(4)	C(3)–O(3)	1.217(4)
C(3)–N(4)	1.376(4)	N(4)–C(5)	1.459(3)
N(4)–N(9)	1.420(3)	C(5)–C(6)	1.521(4)
C(5)–C(12)	1.521(4)	C(6)–C(7)	1.509(4)
C(7)–C(8)	1.523(4)	C(8)–N(9)	1.445(3)
N(10)–N(11)	1.119(5)	C(12)–O(12)	1.205(3)
C(12)–O(13)	1.325(3)	O(13)–C(14)	1.492(3)
C(14)–C(15)	1.496(4)	C(14)–C(16)	1.498(4)
C(14)–C(17)	1.501(5)		

Table 5. Bond angles (°) for (**15g**)

O(1)–C(1)–C(2)	130.5(3)	O(1)–C(1)–N(9)	126.1(3)
C(2)–C(1)–N(9)	103.4(2)	C(1)–C(2)–C(3)	111.0(2)
C(1)–C(2)–N(10)	124.8(3)	C(3)–C(2)–N(10)	124.2(3)
C(2)–C(3)–O(3)	130.4(3)	C(2)–C(3)–N(4)	104.2(2)
O(3)–C(3)–N(4)	125.4(3)	C(3)–N(4)–C(5)	121.2(2)
C(3)–N(4)–N(9)	108.6(2)	C(5)–N(4)–N(9)	114.1(2)
N(4)–C(5)–C(6)	109.4(2)	N(4)–C(5)–C(12)	109.8(2)
C(6)–C(5)–C(12)	113.5(2)	C(5)–C(6)–C(7)	111.8(2)
C(6)–C(7)–C(8)	110.5(2)	C(7)–C(8)–N(9)	108.6(2)
C(1)–N(9)–N(4)	111.5(2)	C(1)–N(9)–C(8)	126.1(2)
N(4)–N(9)–C(8)	116.0(2)	C(2)–N(10)–N(11)	179.3(4)
C(5)–C(12)–O(12)	123.5(2)	C(5)–C(12)–O(13)	110.7(2)
O(12)–C(12)–O(13)	125.8(2)	C(12)–O(13)–C(14)	121.7(2)
O(13)–C(14)–C(15)	109.0(2)	O(13)–C(14)–C(16)	102.7(2)
C(15)–C(14)–C(16)	109.9(3)	O(13)–C(14)–C(17)	110.8(2)
C(15)–C(14)–C(17)	110.9(3)	C(16)–C(14)–C(17)	113.2(3)

95%) in the ratio 1.6:1 by n.m.r., $\nu_{max.}$(neat) 1 770 cm^{-1}; δ_H (250 MHz; $CDCl_3$) for (**18b**) 4.48 (2 H, br s), 4.61 (2 H, s), and 6.9—7.4 (m); for (**19b**) 4.06 (2 H, AB, *J* 12.5 Hz), 4.09 (2 H, AB, *J* 14 Hz), and 6.9—7.4 (m); *m/z* 238 (M^+), 210, 132, 118, 105, 91 (base), and 77.

Photolysis of the Diazo Compound (**15d**).—(a) *In ether and methanol.* A solution of the diazo compound (**15d**) (330 mg) in ether (350 ml) and methanol (30 ml) was irradiated for 4 h. Evaporation of the solvents and chromatography of the residue gave an inseparable mixture of the hydrazone (**20**) and the diazetidinones (**16d**; Nu = MeO) and (**17d**; Nu = MeO) (250 mg), the ratio of the diazetidinones being *ca.* 2.5:1 by n.m.r., δ_H (90 MHz; $CDCl_3$) *inter alia* 1.23 (t), 1.32 (t), 3.47 (AB, *J* 16 Hz), 3.79 (s), 3.82 (s), 3.91 (AB, *J* 18 Hz), 4.0—4.3 (m), 4.40 (AB, *J*, 11.5 Hz), 4.77 (m), 6.78 (s), and 7.35 (m).

(b) *In wet ether.* A solution of the diazo compound (**15d**) (222 mg) in wet ether (250 ml) was irradiated for 4 h. Extractive work-up gave a mixture of 1-benzyl-2-ethoxycarbonylmethyl-

Table 6. Atom co-ordinates (× 10^4) for (**17c**)

Atom	*x*	*y*	*z*
N(1)	674(2)	7 462(3)	3 360(2)
N(2)	1 522(2)	6 320(3)	3 485(2)
C(3)	1 544(2)	6 328(4)	2 593(2)
O(3)	1 997(1)	5 543(3)	2 160(1)
C(4)	722(2)	7 622(4)	2 395(2)
C(5)	1 798(2)	5 201(3)	4 187(2)
C(6)	2 533(2)	4 087(4)	4 150(2)
C(7)	2 834(3)	2 981(5)	4 841(3)
C(8)	2 412(3)	3 000(5)	5 565(3)
C(9)	1 681(3)	4 102(4)	5 604(2)
C(10)	1 370(2)	5 213(4)	4 909(2)
C(11)	1 003(2)	8 972(4)	3 882(2)
C(12)	180(2)	10 207(4)	3 590(2)
C(13)	339(3)	11 612(4)	3 194(3)
C(14)	−415(3)	12 725(4)	2 931(3)
C(15)	−1 351(3)	12 439(4)	3 040(2)
C(16)	−1 519(3)	11 025(5)	3 442(3)
C(17)	−750(3)	9 924(4)	3 725(3)
C(18)	−215(2)	7 161(4)	1 703(2)
O(18)	−928(2)	6 513(4)	1 862(2)
O(19)	−135(1)	7 541(3)	881(2)
C(20)	−986(3)	7 145(5)	114(3)
C(21)	−701(3)	7 530(6)	−721(2)

Table 7. Bond lengths (Å) for (**17c**)

N(1)–N(2)	1.473(3)	N(1)–C(4)	1.488(4)
N(1)–C(11)	1.489(4)	N(2)–C(3)	1.362(4)
N(2)–C(5)	1.392(4)	C(3)–O(3)	1.200(4)
C(3)–C(4)	1.531(4)	C(4)–C(18)	1.493(4)
C(5)–C(6)	1.377(4)	C(5)–C(10)	1.365(4)
C(6)–C(7)	1.376(5)	C(7)–C(8)	1.363(6)
C(8)–C(9)	1.367(6)	C(9)–C(10)	1.384(4)
C(11)–C(12)	1.506(4)	C(12)–C(13)	1.352(5)
C(12)–C(17)	1.362(5)	C(13)–C(14)	1.369(5)
C(14)–C(15)	1.355(6)	C(15)–C(16)	1.366(6)
C(16)–C(17)	1.380(5)	C(18)–O(18)	1.190(4)
C(18)–O(19)	1.317(4)	O(19)–C(20)	1.468(4)
C(20)–C(21)	1.449(6)		

Table 8. Bond angles (°) for (**17c**)

N(2)–N(1)–C(4)	87.6(2)	N(2)–N(1)–C(11)	110.2(2)
C(4)–N(1)–C(11)	111.6(2)	N(1)–N(2)–C(3)	94.6(2)
N(1)–N(2)–C(5)	125.7(2)	C(3)–N(2)–C(5)	134.0(3)
N(2)–C(3)–O(3)	133.2(3)	N(2)–C(3)–C(4)	90.1(2)
O(3)–C(3)–C(4)	136.6(3)	N(1)–C(4)–C(3)	87.3(2)
N(1)–C(4)–C(18)	115.4(3)	C(3)–C(4)–C(18)	115.0(2)
N(2)–C(5)–C(6)	118.6(3)	N(2)–C(5)–C(10)	121.3(3)
C(6)–C(5)–C(10)	120.1(3)	C(5)–C(6)–C(7)	119.9(3)
C(6)–C(7)–C(8)	120.0(3)	C(7)–C(8)–C(9)	120.3(3)
C(8)–C(9)–C(10)	120.2(3)	C(5)–C(10)–C(9)	119.6(3)
N(1)–C(11)–C(12)	107.9(2)	C(11)–C(12)–C(13)	121.6(3)
C(11)–C(12)–C(17)	120.0(3)	C(13)–C(12)–C(17)	118.3(3)
C(12)–C(13)–C(14)	121.1(4)	C(13)–C(14)–C(15)	121.2(4)
C(14)–C(15)–C(16)	118.3(4)	C(15)–C(16)–C(17)	120.3(4)
C(12)–C(17)–C(16)	120.8(4)	C(4)–C(18)–O(18)	125.5(3)
C(4)–C(18)–O(19)	110.2(3)	O(18)–C(18)–O(19)	124.3(3)
C(18)–O(19)–C(20)	117.6(3)	O(19)–C(20)–C(21)	108.1(3)

Table 9. Atom co-ordinates (× 10^4) for (**24**)

Atom	*x*	*y*	*z*
C(1)	898(2)	7 009(2)	5 922(2)
C(2)	907(2)	5 649(3)	6 059(2)
O(2)	351(2)	4 916(2)	6 179(1)
N(3)	1 818(2)	5 584(2)	5 998(1)
C(4)	2 472(2)	4 703(2)	5 853(2)
C(5)	2 493(2)	4 954(2)	4 934(2)
C(6)	2 677(2)	6 274(2)	4 834(2)
C(7)	1 839(2)	7 026(2)	4 935(2)
N(8)	1 924(2)	6 858(2)	5 862(1)
C(9)	3 559(2)	4 691(2)	6 661(2)
O(9)	3 766(2)	5 218(2)	7 360(1)
O(10)	4 226(1)	4 054(2)	6 486(1)
C(11)	5 347(2)	3 929(3)	7 151(2)
C(12)	5 445(3)	3 408(4)	8 038(3)
C(13)	5 850(3)	5 122(4)	7 301(4)
C(14)	5 771(3)	3 080(4)	6 682(3)
C(15)	952(2)	7 779(3)	6 701(2)
O(15)	898(2)	7 357(2)	7 370(1)
N(16)	1 035(2)	8 990(2)	6 627(1)
N(17)	1 272(2)	9 399(2)	5 941(1)
C(18)	1 401(2)	10 533(2)	5 893(2)
C(19)	1 249(2)	11 469(3)	6 485(2)
C(20)	630(3)	10 974(3)	6 957(2)
C(21)	1 025(3)	9 782(3)	7 345(2)
C(22)	1 728(2)	10 976(2)	5 191(2)
O(22)	1 627(2)	12 022(2)	4 980(2)
O(23)	2 152(2)	10 164(2)	4 866(1)
C(24)	2 676(2)	10 502(2)	4 272(2)
C(25)	3 066(4)	9 318(3)	4 105(3)
C(26)	3 578(3)	11 315(4)	4 807(3)
C(27)	1 904(3)	11 037(4)	3 396(2)

Table 10. Bond lengths (Å) for (**24**)

C(1)–C(2)	1.538(4)	C(1)–N(8)	1.501(4)
C(1)–C(15)	1.505(4)	C(2)–O(2)	1.208(4)
C(2)–N(3)	1.334(4)	N(3)–C(4)	1.437(4)
N(3)–N(8)	1.461(3)	C(4)–C(5)	1.531(4)
C(4)–C(9)	1.525(3)	C(5)–C(6)	1.522(4)
C(6)–C(7)	1.517(5)	C(7)–N(8)	1.468(4)
C(9)–O(9)	1.197(4)	C(9)–O(10)	1.306(4)
O(10)–C(11)	1.485(3)	C(11)–C(12)	1.503(6)
C(11)–C(13)	1.482(5)	C(11)–C(14)	1.494(6)
C(15)–O(15)	1.214(4)	C(15)–N(16)	1.371(4)
N(16)–N((17)	1.371(4)	N(6)–C(21)	1.469(4)
N(17)–C(18)	1.290(3)	C(18)–C(19)	1.498(4)
C(18)–C(22)	1.488(5)	C(19)–C(20)	1.494(6)
C(20)–C(21)	1.478(4)	C(22)–O(22)	1.211(3)
C(22)–O(23)	1.318(4)	O(23)–C(24)	1.495(4)
C(24)–C(25)	1.505(5)	C(24)–C(26)	1.498(4)
C(24)–C(27)	1.490(4)		

3-oxo-1,2-diazetidine-4-carboxylic acid (**16d**; Nu = HO) and 2-benzyl-1-ethoxycarbonylmethyl-3-oxo-1,2-diazetidine-4-carboxylic acid (**17d**; Nu = HO) (101 mg, 47%) in the ratio 2.8:1 by n.m.r., $\nu_{max.}$(neat) 3 600—2 450, 1 790, and 1 750 cm^{-1}; δ_H (90 MHz; $CDCl_3$) major isomer 1.23 (3 H, t), 3.84 (2 H, AB, *J* 18 5 Hz), 4.10 (2 H, br s), 4.12 (2 H, q), 4.71 (1 H, s), 7.36 (5 H, s), and 8.39 (1 H, br s, D_2O exch.); for minor isomer 1.23 (3 H, t), 3.56 (2 H, AB, *J* 16.5 Hz), 4.12 (2 H, q), 4.62 (2 H, AB, *J* 15 Hz), 4.78 (1 H, s), 7.36 (5 H, s), and 8.39 (1 H, br s, D_2O exch.).

This mixture of carboxylic acids (48 mg) was dissolved in benzene (10 ml) and heated under reflux for 5 h. Evaporation of the solvent and chromatography of the residue gave (i) 1-*benzyl*-2-*ethoxycarbonylmethyl*-1,2-*diazetidin*-3-*one* (**19c**) (28 mg) as a colourless liquid which could not be completely purified (Found: C, 63.5; H, 6.8; N, 10.8. $C_{13}H_{16}N_2O_3$ requires C, 62.9; H, 6.5; N, 11.3%); $\nu_{max.}$(neat) 1 780 and 1 745 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.26 (3 H, t), 3.82 (2 H, AB *J* 18 Hz), 3.97 (2 H, AB, *J* 12 Hz), 4.17 (2 H, q), 4.18 (2 H, AB, *J* 14 Hz), and 7.34 (5 H, m); *m/z* 248 (M^+), 175, 147, 133, 106, and 91 (base); and (ii) 2-*benzyl*-1-*ethoxycarbonylmethyl*-1,2-*diazetidin*-3-*one* (**18c**) (10 mg) as a colourless liquid (Found: M^+, 248.1155. $C_{13}H_{16}N_2O_3$ requires *M*, 248.1160); $\nu_{max.}$(neat) 1 770 and 1 745 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.21 (3 H, t), 3.42 (2 H, AB, *J* 16 Hz), 4.10 (2 H, q), 4.26 (2 H, AB, *J* 14 Hz), 4.57 (2 H, AB, *J* 16 Hz), and 7.35 (5 H, m); *m/z* 248 (M^+), 192, 175, 162, 147, 118, and 91 (base).

Table 11. Bond angles (°) for (**24**)

C(2)–C(1)–N(8)	87.1(2)	C(2)–C(1)–C(15)	116.8(2)
N(8)–C(1)–C(15)	114.8(2)	C(1)–C(2)–O(2)	137.0(3)
C(1)–C(2)–N(3)	89.5(2)	O(2)–C(2)–N(3)	133.5(3)
C(2)–N(3)–C(4)	139.2(2)	C(2)–N(3)–N(8)	97.0(2)
C(4)–N(3)–N(8)	122.1(2)	N(3)–C(4)–C(5)	108.5(2)
N(3)–C(4)–C(9)	110.0(2)	C(5)–C(4)–C(9)	113.7(3)
C(4)–C(5)–C(6)	111.0(2)	C(5)–C(6)–C(7)	110.6(3)
C(6)–C(7)–N(8)	108.6(2)	C(1)–N(8)–N(3)	86.4(2)
C(1)–N(8)–C(7)	113.5(2)	N(3)–N(8)–C(7)	108.1(2)
C(4)–C(9)–O(9)	123.4(3)	C(4)–C(9)–O(10)	111.6(2)
O(9)–C(9)–O(10)	124.9(2)	C(9)–O(10)–C(11)	122.3(2)
O(10)–C(11)–C(12)	110.9(3)	O(10)–C(11)–C(13)	108.5(3)
C(12)–C(11)–C(13)	110.7(3)	O(10)–C(11)–C(14)	103.1(2)
C(12)–C(11)–C(14)	110.4(3)	C(13)–C(11)–C(14)	112.9(4)
C(1)–C(15)–O(15)	121.8(3)	C(1)–C(15)–N(16)	117.9(3)
O(15)–C(15)–N(16)	120.3(3)	C(15)–N(16)–N(17)	117.5(2)
C(15)–N(16)–C(21)	119.8(3)	N(17)–N(16)–C(21)	122.1(2)
N(16)–N(17)–C(18)	117.8(2)	N(17)–C(18)–C(19)	126.0(3)
N(17)–C(18)–C(22)	118.2(3)	C(19)–C(18)–C(22)	115.8(2)
C(18)–C(19)–C(20)	110.2(2)	C(19)–C(20)–C(21)	110.9(3)
N(16)–C(21)–C(20)	109.8(3)	C(18)–C(22)–O(22)	120.1(3)
C(18)–C(22)–O(23)	114.9(2)	O(22)–C(22)–O(23)	124.9(3)
C(22)–O(23)–C(24)	121.3(2)	O(23)–C(24)–C(25)	102.4(3)
O(23)–C(24)–C(26)	108.3(3)	C(25)–C(24)–C(26)	110.8(3)
O(23)–C(24)–C(27)	110.8(3)	C(25)–C(24)–C(27)	110.8(3)
C(26)–C(24)–C(27)	113.2(3)		

Photolysis of Diazo Compound (**15e**) *in Ether and Methanol.*—A solution of the diazo compound (**15e**) (90 mg) in dry ether (100 ml) and methanol (5 ml) was irradiated for 4 h. Evaporation of the solvents and chromatography of the residue gave an inseparable mixture of the hydrazone (**21**) and the diazetidinones (**16e**; Nu = MeO) and (**17e**; Nu = MeO) (46 mg). From this mixture the *hydrazone* (**21**) could be crystallised as colourless crystals, m.p. 94 °C (Found: C, 46.2; H, 7.8; N, 21.55. $C_5H_{10}N_2O_2$ requires C, 46.1; H, 7.7; N, 21.5%); $\nu_{max.}$(Nujol) 3 300 and 1 690 cm^{-1}. The n.m.r. spectrum of the remaining mixture showed: hydrazone (**21**) δ_H (90 MHz; $CDCl_3$) 1.34 (3 H, t), 2.96 (3 H, d, *J* 5 Hz), 4.29 (2 H, q), 6.68 (1 H, s), and 6.83 (1 H, br s); major diazetidinone (**16e**; Nu = MeO) δ_H 1.28 (3 H, t), 2.82 (3 H, s), 3.88 (3 H, s), 4.11 (2 H, s), 4.22 (2 H, q), and 4.50 (1 H, s); minor diazetidinone (**17e**; Nu = MeO) δ_H 1.28 (3 H, t), 3.10 (3 H, s), 3.70 (2 H, AB, *J* 15 Hz), 3.83 (3 H, s), 4.22 (2 H, q), and 4.76 (1 H, s). The ratio of diazetidinones was *ca.* 2:1.

Photolysis of the Diazo Compound (**15f**) *in Wet Ether.*—A solution of the diazo compound (**15f**) (175 mg) in wet ether (200 ml) was irradiated for 8 h. Extractive work-up gave a colourless oil (67 mg) which could not be identified.

Photolysis of the Diazo Compound (**15g**).—(a) *In ether and ethanol.* A solution of the diazo compound (**15g**) (1.00 g) in dry ether (300 ml) and ethanol (25 ml) was irradiated for 3 h. Evaporation of the solvents and chromatography of the residue

gave (i) diethyl malonate (258 mg, 46%), and (ii) an oily solid from which crystallised, *t-butyl ethyl hexahydro-2-oxo-1,2-diazeto*[1,2-a]*pyridazine-4,1-dicarboxylate* (**16g**; Nu = EtO) (123 mg, 12%) as colourless needles, m.p. 136—138 °C (from ethanol–light petroleum) (Found: C, 56.1; H, 7.5; N, 9.5. $C_{14}H_{22}N_2O_5$ requires C, 56.4; H, 7.4; N, 9.4%); $\nu_{max.}$(Nujol) 1 780, 1 762, and 1 733 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.32 (3 H, t), 1.48 (9 H, s), 1.52—2.00 (3 H, m), 2.24 (1 H, br d, *J* 13.5 Hz), 2.39 (1 H, dt, *J* 13, 2.4 Hz), 3.42 (1 H, dt, *J* 10, 2.4 Hz), 4.29 (2 H, qq), 4.43 (1 H, s), and 4.47 (1 H, d, *J* 6.4 Hz); δ_C (75.5 MHz; $CDCl_3$) 14.2 (q), 20.9 (t), 23.2 (t), 27.9 (q), 53.2 (d), 56.2 (t), 61.9 (t), 80.3 (d), 82.7 (s), 156.3 (s), 164.4 (s), and 167.2 (s); *m/z* 298 (M^+), 242, 197, 169, (base), 141, 114, 97, and 57.

The mother liquors from the above crystallisation were evaporated and the residue recrystallised from light petroleum to give *t-butyl* 1,4,5,6-*tetrahydropyridazine-3-carboxylate* (**23**) (310 mg, 47%), m.p. 92 °C (Found: C, 58.4; H, 9.15; N, 14.9. $C_9H_{16}N_2O_2$ requires C, 58.7; H, 8.75; N, 15.3%); $\nu_{max.}$(Nujol) 3 335, 1 688, and 1 600 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.50 (9 H, s), 1.70—2.16 (2 H, m), 2.40 (2 H, t), 3.19 (2 H, br t), and 6.83 (1 H, br s, D_2O exch.).

(b) *In wet ether.* A solution of the diazo compound (**15g**) (1.30 g) in wet ether (300 ml) was irradiated for 7 h. Hydrogen carbonate extraction and acidification gave *t-butyl hexahydro-2-oxo-1,2-diazeto*[1,2-a]*pyridazine-4-carboxylate-1-carboxylic acid* (**16g**; Nu = HO) (196 mg, 14%), m.p. 109—111 °C, which could not be obtained analytically pure due to its facile decarboxylation, $\nu_{max.}$(Nujol) 3 500—2 500, 1 758, and 1 725 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.47 (9 H, s), 1.58—2.00 (3 H, m), 2.23 (1 H, d, *J* 12.5 Hz), 2.54 (1 H, td, *J* 10, 2.5 Hz), 3.44 (1 H, d, *J* 10 Hz), 4.58 (1 H, s), 4.62 (1 H, d, *J* 7 Hz), and 8.33 (1 H, br s); *m/z* 270 (M^+), 226, 214, 169, 141, 125, 97 (base), 57, and 41. The ether layers from the hydrogen carbonate extraction were evaporated, and the residue chromatographed to give the tetrahydropyridazine (**23**) (360 mg, 48%).

The carboxylic acid (**16**; Nu = HO) (82 mg) was dissolved in benzene (15 ml) and heated under reflux for 2 h. Evaporation of the solvent and chromatography of the residue gave *t-butyl hexahydro-2-oxo-1,2-diazeto*[1,2-a]*pyridazine-4-carboxylate* (**18d**) (11 mg, 16%) as an oil (Found: M^+, 226.1326. $C_{11}H_{18}N_2O_3$ requires *M*, 226.1317); $\nu_{max.}$(neat) 1 765 and 1 735 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.47 (9 H, s), 1.58—1.86 (3 H, m), 2.18 (1 H, d, *J* 12.5 Hz), 2.27 (1 H, m), 3.31 (1 H, dt, *J*, 10, 2.5 Hz), 4.08 (2 H, AB, *J* 13 Hz), and 4.59 (1 H, d, *J* 6.5 Hz); *m/z* 226 (M^+), 142, 125, 97 (base), 85, 83, 57, and 41.

(c) *In dry ether.* A solution of the diazo compound (**15g**) (600 mg) in dry ether (250 ml) was irradiated for 5 h. Evaporation of the ether and chromatography of the residue gave (i) the tetrahydropyridazine (**23**) (210 mg, 51%), and (ii) *t-butyl* 1-[(3-*t-butoxycarbonyl*-1,4,5,6-*tetrahydropyridazin*-1-*yl*)*carbonyl*]-*hexahydro-2-oxo-1,2-diazeto*[1,2-a]*pyridazine-4-carboxylate* (**24**) (130 mg, 11%), m.p. 163 °C (Found: C, 57.7; H, 7.4; N, 12.7. $C_{21}H_{32}N_4O_6$ requires C, 57.8; H, 7.4; N, 12.8%); $\nu_{max.}$(Nujol) 1 778, 1 740, 1 690, and 1 595 cm^{-1}; δ_H (300 MHz; $CDCl_3$) 1.47 (9 H, s), 1.52 (9 H, s), 1.57—2.00 (5 H, m), 2.20 (1 H, br d, *J* 12.5 Hz), 2.47 (3 H, m), 3.76 (3 H, m), 4.62 (1 H, d, *J* 6.5 Hz), and 5.30 (1 H, m); *m/z* 436 (M^+), 380, 307 (base), 279 251, 224, 197, 196, 169, 124, 111, 100, 83, 57, and 41.

Photolysis of the Diazo Compound (**15h**) *in Ether and Ethanol.*—A solution of the diazo compound (**15h**) (24 mg) in ether (100 ml) and ethanol (10 ml) was irradiated for 1.5 h. Evaporation of the solvents gave a mixture of diethyl malonate and a brown gum (19 mg), $\nu_{max.}$ 1 730 cm^{-1} of unknown composition.

Crystal Data.—Compound (**15g**) $C_{12}H_{16}N_4O_4$, *M* = 280.3, monoclinic, *a* = 5.482(1), *b* = 20.108(3), *c* = 12.840(2) Å, β = 95.82(1)°, *U* = 1 409 $Å^3$, μ(Cu-K_α) = 8 cm^{-1}, $\bar{\lambda}$ = 1.541 78 Å, space group $P2_1/n$, *Z* = 4, D_c = 1.32 g cm^{-3}, *F*(000) = 592. Approximate crystal dimensions 0.22 × 0.17 × 0.15 mm; compound (**17c**) $C_{18}H_{18}N_2O_3$, *M* = 310.4, monoclinic, *a* = 13.711(2), *b* = 8.281(1), *c* = 15.172(2) Å, β = 104.31(1)°, *U* = 1 669 $Å^3$, μ(Cu-K_α) = 7 cm^{-1}, $\bar{\lambda}$ = 1.541 78 Å, space group $P2_1/n$, *Z* = 4, D_c = 1.24 g cm^{-3}, *F*(000) = 656. Approximate crystal dimensions 0.30 × 0.30 × 0.15 mm; compound (**24**) $C_{21}H_{32}N_4O_6$, *M* = 436.5, monoclinic, *a* = 14.104(2), *b* = 11.200(2), *c* = 16.217(4) Å, β = 115.69(1)°, *U*2 308 $Å^3$, μ(Cu-K_α) = 7 cm^{-1}, $\bar{\lambda}$ = 1.541 78 Å, space group $P2_1/c$, *Z* = 4, D_c = 1.26 g cm^{-3}, *F*(000) = 936. Approximate crystal dimensions 0.38 × 0.25 × 0.20 mm.

Data Collection and Processing.—Compound (**15g**) 1 452 independent measured reflections (θ ⩽ 50°), 1 290 observed [$|F_o| > 3\sigma(|F_o|)$]; (**17c**) 1 711 independent measured reflections (θ ⩽ 50°), 1 454 observed; compound (**24**) 2 367 independent measured reflections (θ ⩽ 50°), 2 155 observed. All data measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans.

Structure Analysis and Refinement.—All three structures were solved by direct methods and their non-hydrogen atoms refined anisotropically. In structure (**17c**) the position of the C(4) hydrogen atom and in (**24**) the C(1) hydrogen atom were determined from Δ*F* maps and were allowed to refine isotropically. The other hydrogen atom positions, in all three structures, were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters [$U(H) = 1.2U_{eq}(C)$], and allowed to ride on their parent carbon atoms. All the methyl groups were refined as rigid bodies. Refinement was by block-cascade full-matrix least-squares and converged to give for (**15g**) $R = 0.043$, $R_w = 0.048$ ($w^{-1} = \sigma^2(F) + 0.000\,34F^2$), for (**17c**) $R = 0.048$, $R_w = 0.057$ ($w^{-1} = \sigma^2(F) + 0.000\,61F^2$) and for (**24**) $R = 0.046$, $R_w = 0.054$ ($w^{-1} = \sigma^2(F) + 0.000\,49F^2$). Computations were carried out using the SHELXTL program system.

Fractional atomic co-ordinates for the non hydrogen atoms for (**15g**) are given in Table 3. Tables 4 and 5 list the bond lengths and angles respectively. Fractional atomic co-ordinates for (**17c**) are given in Table 6. Tables 7 and 8 list the bond lengths and angles respectively. Fractional atomic co-ordinates for (**24**) are given in Table 9. Tables 10 and 11 list the bond lengths and angles respectively.

The fractional co-ordinates of the hydrogen atoms and isotropic thermal parameters, and the thermal parameters for the non-hydrogen atoms for (**15g**), (**17c**), and (**24**) are available on request from the Cambridge Crystallographic Data Centre.*

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* See Instructions for Authors (1987), para. 5.6.3 in *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

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