Intramolecular Cycloaddition of Azoalkenes Derived from Allylic β-Keto Esters

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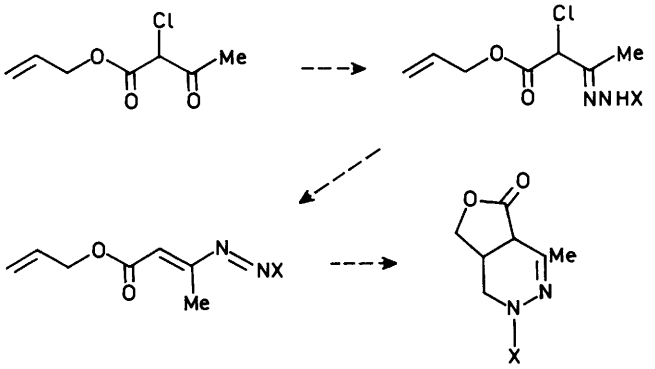
The 2,4-dinitrophenylhydrazone (**2a**) of allyl 2-chloroacetoacetate has been prepared and converted into the azoalkene (**4a**) by reaction with sodium carbonate. The azoalkene undergoes an intramolecular Diels–Alder reaction when heated under reflux in toluene to give a single product, the *cis*-fused lactone (**5a**). Several other allylic esters of ethyl 2-chloroacetoacetate undergo the same sequence of reactions. Evidence is presented that the *cis*-fused lactones are the kinetic products of intramolecular cycloaddition; the reactions are proposed to involve *endo* addition of *E*-azoalkenes. Cyclic azoalkenes (**16**) and (**20**), of the same general type but constrained to the *Z* configuration, have been prepared starting from allyl 2-oxocyclopentane- and allyl 2-oxocyclohexane-1-carboxylates. These also undergo an intramolecular Diels–Alder reaction when heated.

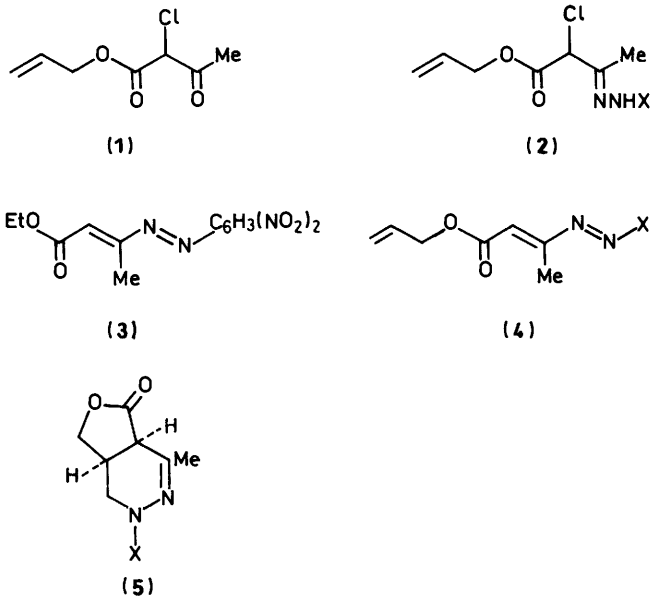
Conjugated azoalkenes bearing an alkoxycarbonyl substituent at the β-position are isolable, and in many cases thermally stable, compounds which undergo a number of different types of cycloaddition reaction. Examples of [2 + 2] and [3 + 2] cycloaddition have been reported,[1] but the most common type of reaction is a [4 + 2] process in which the azoalkene acts as the 4π component. Such reactions normally require electron rich alkenes (enol ethers, *etc.*) as the dienophilic components.[2] We have now investigated intramolecular counterparts of these reactions in which the dienophile is the double bond of an allyloxycarbonyl substituent. This process is outlined in Scheme 1. The objectives of the work have been (i) to determine whether



Scheme 1.

such intramolecular reactions could take place without additional activation of the dienophile and (ii) to determine the stereoselectivity, and hence the preferred geometry, of the transition state. We have shown that intramolecular Diels–Alder reactions of azoalkenes take place readily, and stereoselectively, when the dienophile is attached to the azoalkene through nitrogen.[3] In these intramolecular reactions the dienophile does not require an activating substituent.

The first experiments were carried out on hydrazones of allyl 2-chloroacetoacetate (**1**). The 2,4-dinitrophenylhydrazone (**2a**) and the benzoylhydrazone (**2b**) were isolated, but reaction of the chloro keto ester with phenylhydrazine gave the azoalkene (**4c**) directly. This was obtained as a red crystalline solid. The azoalkene was assigned the *E* configuration, in common with other azoalkenes of this type, on the basis of the chemical shift of the vinylic hydrogen atom. This is at δ 7.05. For comparison we generated ethyl (2,4-dinitrophenylazo)crotonate (**3**) from ethyl chloroacetoacetate 2,4-dinitrophenylhydrazone and sodium

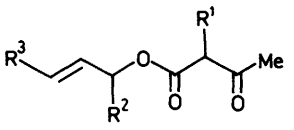


(**2**), (**4**), (**5**) **a**, X = $C_6H_3(NO_2)_2$-2,4
b, X = COPh
(**4**), (**5**) **c**, X = Ph

carbonate. When initially formed the azoalkene was a mixture (1:1) of *E* and *Z* isomers as shown by n.m.r. The vinylic hydrogen atom of the *Z* isomer gave a singal at δ 6.56 and that of the *E* isomer at δ 7.05. After 48 h at room temperature, only the *E* isomer could be detected. Similar reactions of the hydrazones (**2a**) and (**2b**) with sodium carbonate gave the *E*-azoalkenes (**4a**) and (**4b**).

These azoalkenes, though isolable, could be induced to undergo the intramolecular Diels–Alder reaction by heating them in solution. The reactions were most efficiently carried out in toluene under reflux. In each case the reaction was complete after 18 h and only one product could be detected by t.l.c. On the basis of their n.m.r. spectra the cycloadducts were assigned the *cis*-fused lactone structures (**5a**) and (**5b**). The coupling constants for the bridgehead hydrogen atoms (*J* 7.3 and 7.7 Hz respectively) are in accord with *cis*-fused structures. Lactones obtained from other intramolecular Diels–Alder reactions of allylic esters are also reported to be *cis*-fused.[4] The azoalkene (**4c**) was also cyclised by heating in toluene to give an analogous adduct (**5c**) but this was air sensitive and was isolated by chromatography in only moderate yield (31%).

Similar reactions of some related 2,4-dinitrophenylhydrazones were investigated in order to determine the scope of the reaction. Esters (**6a**) and (**6b**) were prepared from diketene and the appropriate alcohol. These were then chlorinated to give the esters (**7**) from which the dinitrophenylhydrazones (**8**) were prepared and dehydrochlorinated as before. The azoalkene (**9a**) could *not be isolated*; it cyclised spontaneously at room temperature to give the adduct (**10a**). Evidently the terminal phenyl substituent has a significant activating effect on the double bond, as has been observed before in intermolecular reactions of azoalkenes.[5] The azoalkene (**9b**) was isolated and



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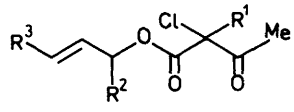

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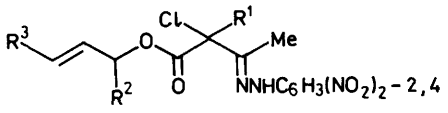

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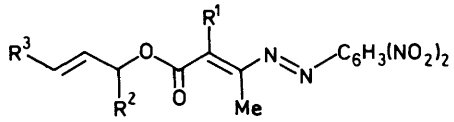

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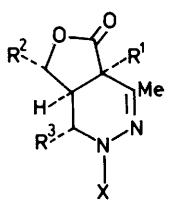

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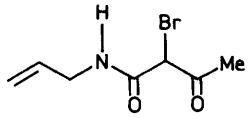

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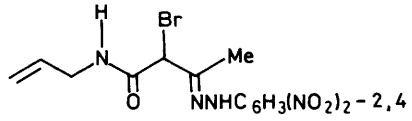

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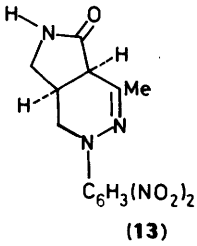


(13)

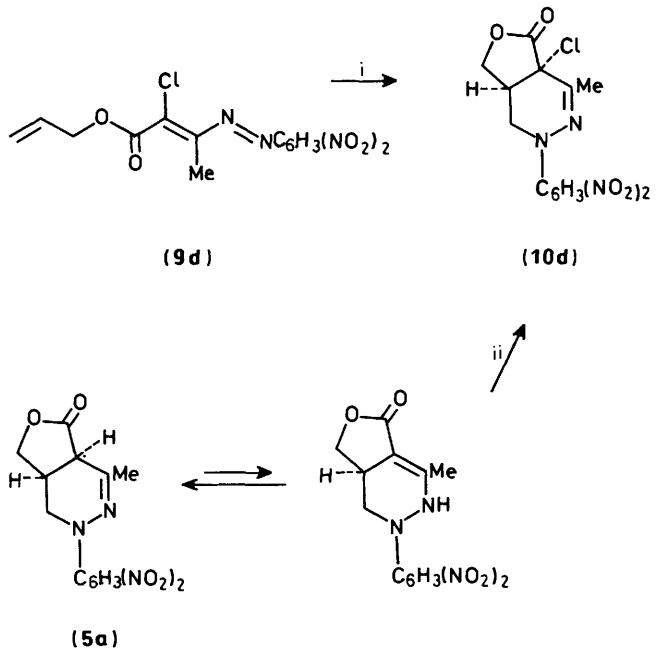
(6)—(10) **a**, $R^1 = R^2 = H$, $R^3 = Ph$
b, $R^1 = R^3 = H$, $R^2 = Me$
c, $R^1 = Me$, $R^2 = H$, $R^3 = Ph$
(7)—(10) **d**, $R^1 = Cl$, $R^2 = R^3 = H$

was then cyclised by heating in toluene. Despite the presence of an additional asymmetric carbon atom, this reaction gave a single product, to which the structure (**10b**) was assigned on the basis of its n.m.r. spectrum. Attempts to observe similar intramolecular Diels–Alder reactions starting from prop-2-ynyl or but-3-enyl esters of acetoacetic acid were, however, unsuccessful: the azoalkenes could be prepared in the same way but they failed to cyclise on heating in solution. An analogous fused lactam, compound (**13**), was prepared by way of the acetoacetamide (**11**) and its 2,4-dinitrophenylhydrazone (**12**).

Although these reactions were apparently highly stereoselective it remained to be established that we were isolating the kinetic products. Compounds (**5**), (**10a**), (**10b**), and (**12**) all have acidic hydrogen atoms at position 4a, as was shown by observing deuterium exchange when compound (**10a**) was dissolved in deuteriomethanol. Thus, although we could detect only one cyclisation product in each case, it seemed possible that a less stable *trans*-fused lactone, or a mixture of the two, was formed initially but then isomerized when subjected to chromatography. In order to remove this possibility we required to isolate similar cycloadducts with substituents other than hydrogen at position 4a.

The cinnamyl ester (**9c**), in which the vinylic hydrogen of (**9a**) has been replaced by methyl, was prepared for this purpose. Cinnamyl acetoacetate was methylated to give the ester (**6c**) which was then converted into the 2,4-dinitrophenylhydrazone (**8c**) as before. When this was treated with sodium carbonate it gave the azoalkene (**9c**) which cyclised at room temperature to give the adduct (**10c**) in high yield. The *cis*-fused structure of this adduct was supported by the observation of n.O.e. enhancements both for the adjacent bridgehead hydrogen atom attached to C-7a and for the *ortho* hydrogens of the phenyl group at C-9.

Further evidence in support of the formulation of the *cis*-fused lactones as the kinetic products was obtained as follows. Allyl 2,2-dichloroacetoacetate was converted into its 2,4-dinitrophenylhydrazone (**8d**). This gave the azoalkene (**9d**) with sodium carbonate. When heated in toluene this gave a single cycloadduct, which is formulated as (**10d**). The same compound (**10d**) was also produced by the chlorination of the lactone (**5a**) using sulphuryl chloride (Scheme 2). From models it appears

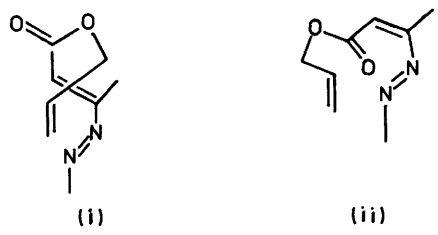


(9d) (10d) (5a)

Scheme 2. *Reagents:* i, 110 °C; ii, SO_2Cl_2

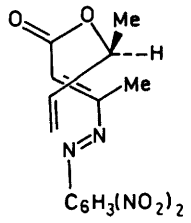
likely that chlorination from the less hindered face of the enamine tautomer of (**5a**) will result in the formation of the *cis*-fused lactone (**10d**).

We conclude on the basis of these results that the intramolecular Diels–Alder reactions of these azoalkenes proceed stereoselectively to give *cis*-fused adducts as the kinetic products. Two transition states are possible for such a process: (i) reaction of the *E* azoalkene with *endo* approach of the diene to the dienophile and (ii) reaction of the *Z* azoalkene with *exo*



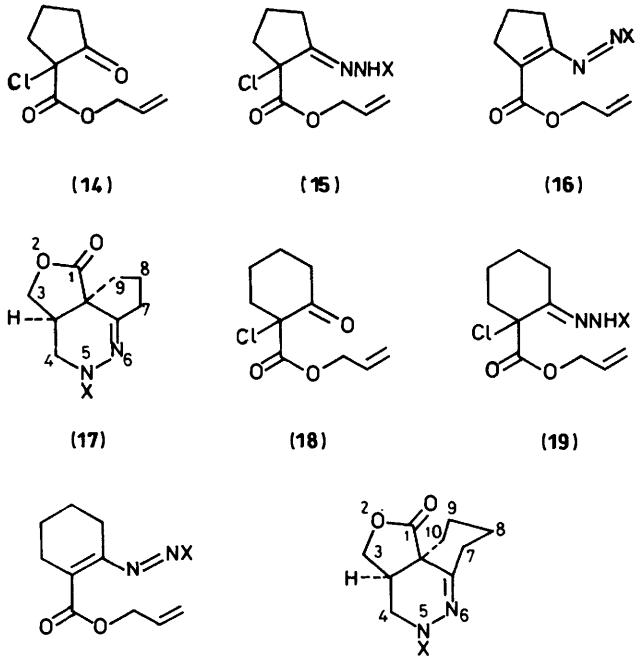
(i) (ii)

Figure 1.



(2)

Figure 2.



(14) (15) (16)

(17) (18) (19)

(20) (21)

(15),(16),(17),(19),(20),(21) a; X = $C_6H_3(NO_2)_2$-2,4
b; X = CO_2Bu^t
(16),(17),(20),(21) c; X = Ph

approach of the diene to the dienophile (Figure 1). Reaction of the *E* azoalkene through an *exo* transition state, which was observed in the azoalkene additions studied earlier,[3] is ruled out in this case because it would lead to *trans*-fused cycloadducts. Of the two possibilities, transition state (i) seems much more likely since, as we have shown, these azoalkenes show a strong preference for the *E* configuration. The preference for the *endo* mode of addition may be steric in origin, since in the *exo* mode there is the likelihood of non-bonded interaction between the methyl group at C-3 of the azoalkene and the carbonyl group of the ester. This transition state also accounts for the stereoselectivity of the cycloaddition of the but-3-en-2-yl ester (**9b**), since only one arrangement of the side chain avoids a severe steric interaction between the methyl group of the linking chain and that attached to the heterodiene (Figure 2). From models the failure of the prop-2-ynyl and but-3-enyl esters to undergo cycloaddition is also explicable on steric grounds: in both cases the *endo* transition states are strained.

Although transition state (i) was the more likely for the reasons stated, we wished to determine whether the alternative (ii) was feasible. A simple way of testing this is to constrain the azoalkene to the *Z* configuration by incorporating the C=C bond into a ring. Accordingly two cyclic β-keto esters, allyl 2-oxocyclopentane-1-carboxylate and allyl 2-oxocyclohexane-1-carboxylate, were prepared by literature methods. Chlorination gave the esters (**14**) and (**18**) respectively. Three azoalkenes (**16a**—**c**) and (**20a**—**c**) were prepared from each by reaction with 2,4-dinitrophenylhydrazine, t-butoxycarbohydrazide, and phenylhydrazine. These azoalkenes all proved to be noticeably more stable to heat than their acyclic counterparts, especially those derived from the six-membered ring ester. All cyclised slowly but cleanly when heated in toluene or xylene to give, in each case, a single product. Thus, the azoalkene (**16a**) required heating for 48 h in toluene to effect cyclisation and it gave an adduct, which was formulated as (**17a**), in good yield (70%). The t-butoxycarbonyl derivative (**16b**) cyclised more rapidly, reaction being complete after 8 h in toluene under reflux. At the other extreme, the phenyl substituted azoalkene (**20c**) required heating for 8 days in xylene before reaction was complete, but the adduct (**21c**) was still isolated in fairly good yield (60%). There was a qualitative parallel between the rate of cycloaddition and the electron-withdrawing effect of the nitrogen substituent of the azoalkene. Since there is only one accessible transition state for these cycloadditions and no acidic hydrogen to allow epimerisation, the structures (**17**) and (**21**) are assigned on this basis.

There are thus probably two modes of intramolecular Diels–Alder reaction of these azoalkenes, the lower energy one [Type (i)] operating with flexible azoalkenes and the other [Type (ii)] being the only one available to azoalkenes which are constrained to the *Z* configuration. Both lead to the formation of cycloadducts in good yield and with high stereoselectivity.

Experimental

I.r. spectra were recorded for KBr discs (solids) or for films (oils) on a Perkin-Elmer 125 spectrophotometer. ^1H N.m.r. spectra were recorded using a 220 MHz Perkin-Elmer R34 spectrometer, or a 250 MHz Bruker WM250 spectrometer with deuteriochloroform as solvent, unless otherwise indicated. Flash column chromatography was performed by the method described by Still *et al.*[6] with Merck 9385 silica gel as the stationary phase. Ether refers to diethyl ether and light petroleum refers to the fraction boiling 60—80 °C.

Allyl acetoacetate was obtained from the Aldrich Chemical Company Ltd. Cinnamyl acetoacetate (**6a**)[7] and but-3-en-2-yl acetoacetate (**6b**)[7] were prepared from diketene and the appropriate alcohol.[8] Allyl 2-oxocyclopentanecarboxylate was obtained from diallyl adipate, and allyl 2-oxocyclohexanecarboxylate from diallyl pimelate, by the method of Tsuji *et al.*[9] *N*-Allylacetoacetamide was prepared from diketene and allylamine by the literature procedure.[10]

Cinnamyl 2-Methylacetoacetate (**6c**).—This ester was prepared (72%) from cinnamyl acetoacetate, pyrrolidine, and iodomethane by the method described by Stiles, Wolf, and Hudson.[11] It was isolated as an oil, b.p. 250 °C (bath) at 1.5 mmHg; $\nu_{max.}$(film) 1 745, 1 715 (C=O), and 1 600 (C=C) cm^{-1};

Table 1. Analytical data for 2,4-dinitrophenylhydrazones (DNPs) of chloro esters

Ester	DNP (Formula)	Yield (%)	Solvent	M.p. (°C)	Found (%) (Required) C	H	N
(1)	(2a) $C_{13}H_{13}ClN_4O_6$	65	Ether–hexane	71	43.5 (43.8	3.9 3.7	15.6 15.7)
(7a)	(8a) $C_{19}H_{17}ClN_4O_6$	74	Dichloromethane–hexane	118–120	52.4 (52.7	4.1 3.9	12.7 12.95)
(7b)	(8b)	91	*a*				
(7c)	(8c) $C_{20}H_{19}ClN_4O_6$	67	Dichloromethane–hexane	137–140	51.6 (51.3	4.1 4.3	12.65 12.5)
(7d)	(8d) $C_{13}H_{12}CL_2N_4O_6$	91	Dichloromethane–hexane	103–108	40.0 (39.9	3.1 3.1	14.4 14.3)
(14)	(15a) $C_{15}H_{15}ClN_4O_6$	67	Ethyl acetate–pentane	126–129	47.0 (47.05	3.9 3.9	14.2 14.5)
(18)	(19a) $C_{16}H_{17}ClN_4O_6$	67	Ether	127–129	48.4 (48.4	4.4 4.3	14.4 14.1)

[a] Oil; characterised only by i.r. and n.m.r.: $\nu_{max.}$(film) 3 320 (NH) and 1 745 (C=O) cm^{-1}; δ(220 MHz) 1.45 (3 H, d, *J* 6.4 Hz), 2.25 (3 H), 5.30—5.45 (2 H, m), 5.55 (1 H, q), 5.80—6.00 (1 H, m), 7.95 (1 H, d), 8.35 (1 H, dd), and 9.10 (1 H, d).

δ(220 MHz) 1.33 (3 H, d, *J* 7.2 Hz), 2.17 (3 H), 3.49 (1 H, q), 4.72 (2 H, d, *J* 7.8 Hz), 6.22 (1 H, dt), 6.81 (1 H, d, *J* 15.6 Hz), and 7.04—7.35 (5 H, m). The compound was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 99—101 °C (from dichloromethane–light petroleum) (Found: C, 58.0; H, 4.8; N, 13.7. $C_{20}H_{20}N_4O_6$ requires C, 58.2: H, 4.9; N, 13.6%).

Chlorination of β-Keto Esters: General Procedure.[12]—To a solution of the ester (0.1 mol) in dry dichloromethane (20 ml) at 0 °C was added dropwise during 3 h a solution of sulphuryl chloride (0.025 mol) in dichloromethane (15 ml). Dry nitrogen was bubbled through the solution during the addition. At the end of this period more sulphuryl chloride [0.075 mol in dichloromethane (45 ml)] was added slowly and the solution was left for a further 12 h at 0 °C, then for 4 h at room temperature. The solution was then washed with an excess of aqueous sodium hydrogen carbonate and water, dried, and evaporated under reduced pressure. In cases where the chloro ester was thermally stable it was then purified by bulb-to-bulb distillation.

The following were prepared by this method. (a) Allyl 2-chloroacetoacetate (**1**)[12] (91%); $\nu_{max.}$(film) 1 740 and 1 720 cm^{-1} (C=O); δ(220 MHz) 2.40 (3 H), 4.73—4.80 (2 H, d, *J* 7 Hz), 5.07 (1 H), 5.29—5.47 (2 H, m), and 5.87—6.08 (1 H, m).

(b) Cinnamyl 2-chloroacetoacetate (**7a**)[12] (82%), b.p. 189 °C (bath) at 0.1 mmHg; $\nu_{max.}$(film) 1 745 and 1 720 cm^{-1} (C=O); δ(220 MHz) 2.37 (3 H), 4.77 (1 H), 4.85 (2 H, d, *J* 6.7 Hz), 6.17 (1 H, dt), 6.72 (1 H, d, *J* 13.9 Hz), and 7.17—7.47 (5 H, m).

(c) *But-3-en-2-yl 2-chloroacetoacetate* (**7b**) (90%), b.p. 150 °C (bath) at 0.08 mmHg (Found: C, 49.9; H, 5.7. $C_8H_{11}ClO_3$ requires C, 50.4: H, 5.8%); $\nu_{max.}$(film) 1 740 and 1 710 cm^{-1} (C=O); δ(250 MHz) 1.38 (3 H, d, *J* 6.8 Hz), 2.37 (3 H), 4.84 (1 H), 5.20 (1 H, d, *J* 10.4 Hz), 5.31 (1 H, d, *J* 17.3 Hz), 5.45 (1 H, q, *J* 6.8 Hz), and 5.75—6.00 (1 H, m).

(d) Cinnamyl 2-chloro-2-methylacetoacetate (**7c**) (58%), b.p. 250 °C (bath) and 2 mmHg; $\nu_{max.}$(film) 1 730 and 1 710 (C=O) and 1 600 (C=C) cm^{-1}; δ(220 MHz) 1.83 (3 H), 2.37 (3 H), 4.85 (2 H, d, *J* 6.1 Hz), 6.30 (1 H, dt), 6.82 (1 H, d, *J* 16.7 Hz), and 7.20—7.45 (5 H, m).

(e) Allyl 2,2-dichloroacetoacetate (**7d**) (68%) [prepared using sulphuryl chloride (0.2 mol) and allyl acetoacetate (0.1 mol)], b.p. 160 °C (bath) and 0.3 mmHg; $\nu_{max.}$(film) 1 740 and 1 720 cm^{-1} (C=O); δ(220 MHz) 2.45 (3 H), 4.75 (2 H, d, *J* 6.7 Hz), 5.25—5.45 (2 H, m), and 5.80—6.00 (1 H, m). This ester is not stable to storage at room temperature in air.

(f) *Allyl 1-chloro-2-oxocyclopentanecarboxylate* (**14**) (97%), b.p. 170 °C (bath) and 0.1 mmHg (Found: C, 52.7; H, 5.5. $C_9H_{11}ClO_3$ requires C, 53.3: H, 5.4%); $\nu_{max.}$(film) 1 760 and 1 720 cm^{-1} (C=O); δ(220 MHz) 2.08—2.25 (2 H, m), 2.33—2.65 (2 H, m), 2.70—2.83 (2 H, m), 4.70 (2 H, d, *J* 5.5 Hz), 5.24—5.38 (2 H, m), and 5.82—5.98 (1 H, m); *m/z* 204, 202 (M^+), and 133 (base).

(g) *Allyl 1-chloro-2-oxocyclohexanecarboxylate* (**18**) (90%) which was purified by flash chromatography (ether) (Found: C, 55.5; H, 6.2. $C_{10}H_{13}ClO_3$ requires C, 55.4: H, 6.1%); $\nu_{max.}$(film) 1 730 and 1 720 cm^{-1} (C=O); δ(250 MHz) 1.69—2.17 (4 H, m), 2.18—2.50 (2 H, m), 2.75—2.92 (2 H, m), 4.73 (2 H, d, *J* 6.1 Hz), 5.29 (1 H, dd, *J* 10.0 and 1.5 Hz), 5.38 (1 H, dd, *J* 17.3 and 1.5 Hz), and 5.85—6.01 (1 H, m); *m/z* 218 and 216 (M^+).

N-*Allyl-2-bromoacetoacetamide* (**11**).—*N*-Bromosuccinimide (5.34 g, 0.03 mol) was added to a solution of *N*-allylacetoacetamide (4.23 g, 0.03 mol) in dry acetone (20 ml) at room temperature during 3 h. The reaction mixture was filtered to remove succinimide and the filtrate was evaporated to dryness. The residue was extracted with hexane and the hexane solution was washed with water, dried, and evaporated. The residue was distilled at 250 °C (bath) and 1.0 mmHg to give the *amide* (**11**) (6.06 g, 92%) as an oil [Found: *m/z* 220.9887 (M^+). $C_7H_{10}BrNO_2$ requires 220.9874]; $\nu_{max.}$(film) 3 060 (NH), 1 730 (C=O), and 1 650 (C=O) cm^{-1}; δ(250 MHz) 2.43 (3 H), 3.93 (2 H, t, *J* 5.1 Hz), 4.85 (1 H), 5.17—5.28 (2 H, m), 5.77—5.96 (1 H, m), and 6.98 (1 H, br, NH).

2,4-*Dinitrophenylhydrazones: General Procedure.*—The halogenated ester or amide (0.1 mol) was added to a solution of 2,4-dinitrophenylhydrazine (0.1 mol) in tetrahydrofuran (5 ml) containing 3 drops of conc. HCl. The mixture was stirred for 24 h at room temperature then the solvent was distilled off. The residue was crystallised from the solvent specified.

The 2,4-dinitrophenylhydrazones of chloro esters which were prepared by this method are listed in Table 1.

N-*Allyl-2-bromoacetoacetamide* 2,4-*Dinitrophenylhydrazone* (**12**).—This compound, which was prepared (60%) by the general method described above for the chloro esters, had m.p. 113—118 °C (from ether–light petroleum) (Found: C, 39.1; H, 3.5; N, 17.45. $C_{13}H_{14}BrN_5O_5$ requires C, 39.0: H, 3.5; N, 17.5%); $\nu_{max.}$(KBr) 3 311 (NH) and 1 662 (C=O) cm^{-1}; δ(250 MHz) 2.19 (3 H), 3.95—4.45 (2 H, m), 5.21 (1 H, d, *J* 6.2 Hz), 5.28 (1 H, d, *J*

14.4 Hz), 5.29 (1 H), 5.82—5.97 (1 H, m), 6.77 (1 H, br, NH), 7.96 (1 H, d, *J* 9.4 Hz), 8.33 (1 H, dd), 9.14 (1 H, d, *J* 2.4 Hz), and 11.13 (1 H, NH).

Allyl 2-Chloroacetoacetate Benzoylhydrazone (**2b**).—Allyl 2-chloroacetoacetate (**1**) (1.76 g, 10.0 mmol) was added to a suspension of benzohydrazide (1.36 g, 10.0 mmol) in ether (10 ml) containing a drop of conc. HCl. The mixture was stirred for 2 h and the solvent was then distilled off. The residue was triturated with ether and filtered. The filtrate was evaporated to leave the crude hydrazone (**2b**) (1.92 g, 65%) as a yellow oil; δ(220 MHz) 2.10 (3 H), 4.55—4.90 (2 H, m), 5.20—5.45 (3 H, m), 5.75—6.05 (1 H, m), 7.36—7.60 (3 H, m), 7.75—7.85 (2 H, m), and 9.10 (1 H, br, NH); *m/z* (chemical ionisation, NH_3 gas) 314 and 312 ($M^+ + NH_3 + 1$). The hydrazone was not purified further.

Allyl 1-Chloro-2-oxocyclopentanecarboxylate t-Butoxycarbonylhydrazone (**15b**).—The chloro ester (**14**) (2.02 g, 0.01 mmol) and t-butoxycarbohydrazide (1.32 g, 0.01 mol) were stirred together in ether (15 ml) containing acetic acid (2 drops) for 24 h. The solvent was then distilled off to leave a solid. Crystallisation gave the *hydrazone* (**15b**) (2.24 g, 72%), m.p. 109—110 °C (from ether–light petroleum) (Found: C, 53.3; H, 6.9; N, 8.9. $C_{14}H_{21}ClN_2O_4$ requires C, 53.1: H, 6.8; N, 8.85%; $\nu_{max.}$(KBr) 3 225 (NH), 1 755 (C=O), and 1 705 (C=O) cm^{-1}; δ(250 MHz) 1.49 (9 H), 2.08—2.19 (2 H, m), 2.23—2.37 (2 H, m), 2.46—2.69 (2 H, m), 4.74 (2 H, d, *J* 5.5 Hz), 5.27 (1 H, d, *J* 10.6 Hz), 5.41 (1 H, d, *J* 17.3 Hz), 5.83—6.01 (1 H, m), and 7.53 (1 H, br, NH).

Allyl 1-Chloro-2-oxocyclohexanecarboxylate t-Butoxycarbonylhydrazone (**19b**).—The chloro ester (**18**) (0.01 mol) gave, by the method described for the preceding compound, the *hydrazone* (**19b**) (1.98 g, 60%), m.p. 145—148 °C (from ether–light petroleum) (Found: C, 54.4; H, 7.05; N, 8.4. $C_{15}H_{23}ClN_2O_4$ requires C, 54.4: H, 7.1; N, 8.4%); $\nu_{max.}$(KBr) 3 230 (NH) and 1 730 (C=O) cm^{-1}; δ(250 MHz) 1.48 (9 H), 1.55—1.99 (4 H, m), 2.10—2.40 (2 H, m), 2.50—2.58 (2 H, m), 4.76 (2 H, d, *J* 5.5 Hz), 5.25 (1 H, dd, *J* 10.2 and 1.1 Hz), 5.38 (1 H, dd, *J* 17.0 and 1.1 Hz), 5.95—6.08 (1 H, m), and 8.30 (1 H, br, NH).

(E)-*Allyl 3-(Phenylazo)crotonate* (**4c**).—This compound was prepared from allyl 2-chloroacetoacetate by the general method of van Alphen.[13] A mixture of sodium acetate (7.8 g, 9.5 mmol) in water (30 ml) and phenylhydrazine (6.15 g, 5.7 mmol) in ethanol (100 ml) was added rapidly with stirring to a solution of the ester (**1**) (10.1 g, 5.7 mmol) in ethanol (60 ml). After 1 h the reaction mixture was filtered to give the *azoalkene* (**4c**) (9.6 g, 73%) as a red solid, m.p. 34 °C (from ethanol) (Found: C, 67.5; H, 6.1; N, 12.4. $C_{13}H_{14}N_2O_2$ requires C, 67.8: H, 6.1; N, 12.2%); $\nu_{max.}$(KBr) 1 710 cm^{-1} (C=O); δ(250 MHz) 2.33 (3 H), 4.69—4.77 (2 H, d, *J* 7.0 Hz), 5.27—5.42 (2 H, m), 5.85—6.05 (1 H, m), 7.05 (1 H), 7.45—7.55 (2 H, m), 7.60—7.70 (2 H, m), and 7.90—7.95 (2 H, m); *m/z* 258 (M^+), 205, 161, and 105 (base).

Allyl 2-(Phenylazo)cyclopentene-1-carboxylate (**16c**).—The chloro ester (**14**) gave, by the method described for the preceding compound, the azoalkene (**16c**) (98%) as a red oil; δ(220 MHz) 1.10—1.50 (2 H, m), 1.70—2.30 (2 H, m), 2.50—3.10 (2 H, m), 4.60 (2 H, t, *J* 6.0 Hz), 5.10—5.20 (2 H, m), 5.85—6.30 (1 H, m), 7.20—7.46 (3 H, m), and 7.67—7.90 (2 H, m). The compound was not fully characterised.

Allyl 2-(Phenylazo)cyclohexene-1-carboxylate (**20c**).—The chloro ester (**18**) gave, by the method described for compound (**4c**), the *azoalkene* (**20c**) (88%) as a red oil (Found: C, 70.7; H, 6.9; N, 9.8. $C_{16}H_{18}N_2O_2$ requires C, 70.7: H, 6.8: N, 9.4%); $\nu_{max.}$(film) 1 725 (C=O) and 1 640 (C=C) cm^{-1}; δ(250 MHz) 1.78 (4 H, br s), 2.47 (2 H, br s), 2.65 (2 H, br s), 4.77 (2 H, d, *J* 5.9 Hz), 5.25 (1 H, d, *J* 10.2 Hz), 5.37 (1 H, d, *J* 17.1 Hz), 5.92—6.05 (1 H, m), 7.39—7.43 (3 H, m), and 7.71—7.74 (2 H, m); *m/z* 270 (M^+), 212, 105, and 77 (base).

Table 2. N.m.r. data for 3-(2,4-dinitrophenylazo)crotonates

DNP Azoalkene	(**2**) (**4a**) (*E*)[a]	(**2**) (**4a**) (*Z*)[a]	(**8b**) (**9b**) (*E*)	(**8d**) (**9d**) (*Z*)
δ(3-Me)	2.45	2.15	2.40	2.19
δ(2-H)	7.05	6.62	7.08	—

[a] Initially isolated as a mixture (5:2) of *E*- and *Z*-isomers.

Allyl 3-(Benzoylazo)crotonate (**4b**).—Sodium carbonate (5 g) was added to a solution of the benzoylhydrazone (**2b**) (1.5 g, 5.1 mmol) in dichloromethane (150 ml) and the mixture was stirred for 4 h. The solid was filtered off and the filtrate was evaporated to dryness. Flash chromatography gave [with ether–hexane (1:1)] the *azoalkene* (**4b**) (0.70 g, 53%) as a red oil [Found: *m/z* 258.1014 (M^+). $C_{14}H_{14}N_2O_3$ requires 258.1004]; $\nu_{max.}$(film) 1 720 cm^{-1} (C–O); δ(220 MHz) 2.53 (3 H), 4.73 (2 H, d, *J* 7.0 Hz), 5.27—5.42 (2 H, m), 5.85—6.05 (1 H, m), 7.05 (1 H), 7.45—7.70 (3 H, m), and 7.90—7.95 (2 H, m).

2,4-*Dinitrophenylazoalkenes*.—(a) *Generation and isomerisation of ethyl 3-(2,4-dinitrophenylazo)crotonate* (**3**). Ethyl chloroacetoacetate 2,4-dinitrophenylhydrazone (1.0 g) was dissolved in dichloromethane (50 ml) and the solution was stirred for 24 h with sodium carbonate (2.0 g). The reaction mixture was filtered and the filtrate was evaporated to leave a red oil, which was shown by n.m.r. to be a mixture (1:1) of *E*- and *Z*-isomers; δ(220 MHz) 2.11 (3-Me of *Z*-isomer), 2.36 (3-Me of *E*-isomer), 6.56 (2-H of *Z*-isomer) and 7.05 (2-H of *E*-isomer). After 2 days at room temperature it had isomerised to the *E-isomer* of (**3**), m.p. 79—80 °C (from ethanol) (Found: C, 46.6; H, 3.9; N, 17.95. $C_{12}H_{12}N_4O_6$ requires C, 46.8; H, 3.9; H, 3.9; N, 18.2%); δ(220 MHz) 1.37 (3 H, t), 2.36 (3 H), 4.32 (2 H, q), 7.05 (1 H), 7.75 (1 H, d), 8.52 (1 H, dd), and 8.77 (1 H, d).

(b) *Other 3-(2,4-dinitrophenylazo)crotonates*. By a similar method the azoalkenes listed in Table 2 were isolated and identified by n.m.r. spectroscopy. All were obtained as red oils and they were not fully characterised.

(c) *Allyl 2-(2,4-dinitrophenylazo)cyclopent-1-ene-1-carboxylate* (**16a**). The 2,4-dinitrophenylhydrazone (**15a**) (0.76 g, 1.9 mmol) gave, by the procedure described in (a), the azoalkene (**16a**) (0.63 g, 92%) as a red oil; δ(220 MHz) 2.07—2.11 (2 H, m), 2.72—2.76 (2 H, m), 2.98—3.02 (2 H, m), 4.77 (2 H, d, *J* 7.3 Hz), 5.24—5.44 (2 H, m), 5.89—6.00 (1 H, m), 7.77 (1 H, d), 8.47 (1 H, dd), and 8.72 (1 H, d). It was not characterised further.

(d) *Allyl 2-(2,4-dinitrophenylazo)cyclohex-1-ene-1-carboxylate* (**20a**). A solution of the 2,4-dinitrophenylhydrazone (**19a**) (0.80 g, 2.01 mmol) in dichloromethane (100 ml) was stirred with sodium hydrogen carbonate (2.5 g) for 24 h. The reaction mixture was filtered and the filtrate was evaporated to leave a red solid (0.71 g, 98%). Crystallisation gave the *azoalkene* (**20a**), m.p. 115—116 °C (from dichloromethane–hexane) (Found: C, 53.3; H, 4.5: N, 15.5. $C_{16}H_{16}N_4O_6$ requires C, 53.3: H, 4.4; N, 15.55%); $\nu_{max.}$(KBr) 1 719 (C=O) and 1 623 (C=C) cm^{-1}; δ(250 MHz) 1.81 (4 H, br s), 2.42 (2 H, br s), 2.69 (2 H, br s), 4.78 (2 H, d, *J* 5.7 Hz), 5.29 (1 H, d, *J* 10.2 Hz), 5.38 (1 H, d, *J* 17.5 Hz), 5.91—6.06 (1 H, m), 7.57 (1 H, d, *J* 8.7 Hz), 8.43 (1 H, dd), and 8.74 (1 H, d, *J* 2.2 Hz).

Allyl 2-(*t-Butoxycarbonylazo*)*cyclopent*-1-*ene*-1-*carboxylate* (**16b**).—Sodium carbonate (4.5 g) was added to a suspension of the hydrazone (**15b**) (1.5 g, 4.7 mmol) in dichloromethane (150 ml). The mixture was stirred for 18 h and filtered. The filtrate was evaporated to leave the azoalkene (1.27 g, 89%) as an orange oil; δ(250 MHz) 1.60 (9 H), 2.00—2.10 (2 H, m), 2.75—2.85 (2 H, m), 2.95—3.05 (2 H, m), 4.77 (2 H, d, *J* 5.9 Hz), 5.20—5.50 (2 H, m), and 5.98—6.05 (1 H, m). The compound was not characterised further.

Allyl 2-(*t-Butoxycarbonaylazo*)*cyclohex*-1-*ene*-1-*carboxylate* (**20b**).—By the method described for the preceding compound the hydrazone (**19b**) (0.89 g, 2.69 mmol) gave the azoalkene (**20b**) (0.71 g, 90%) as an orange oil; δ(250 MHz) 1.60 (9 H), 1.70—1.80 (4 H, m), 2.25—2.35 (2 H, m), 2.72—2.80 (2 H, m), 4.75 (2 H, d, *J* 5.7 Hz), 5.20—5.45 (2 H, m), and 5.85—6.05 (1 H, m). The compound was not characterised further.

2-(2,4-*Dinitrophenyl*)-4-*methyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one* (**5a**).—A solution of the azoalkene (**4a**) 2.0 g, 6.3 mmol) in toluene (150 ml) was heated under reflux under N_2 for 18 h. The solvent was distilled off and the solid residue was subjected to flash chromatography, which gave (with ethyl acetate) the *pyridazinone* (**5a**) (1.8 g, 90%), m.p. 198—205 °C (from ethyl acetate–hexane) (Found: C, 48.6; H, 3.8; N, 17.5. $C_{13}H_{12}N_4O_6$ requires C, 48.75: H, 3.9; N, 17.5%); $\nu_{max.}$(KBr) 1 780 cm^{-1}; δ(250 MHz, $CDCl_3$–CF_3CO_2H) 2.27 (3 H), 3.22—3.28 (2 H, m, 7a-H and 1-H), 3.49 (1 H, d, *J* 7.3 Hz, 4a-H), 3.85—3.95 (1 H, m, 1′-H), 4.40 (1 H, dd, $J_{77'}$ 9.9 Hz, J_{77a} 2.2 Hz, 7-H), 4.68 (1 H, dd, $J_{7'7a}$ 5.8 Hz, 7′-H), 7.35 (1 H, d, *J* 9.2 Hz), 8.37 (1 H, dd), and 8.63 (1 H, d, *J* 2.4 Hz); *m/z* 320 (M^+, base) and 303.

2-*Benzoyl*-4-*methyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one* (**5b**).—A solution of the azoalkene (**4b**) (0.70 g, 2.7 mmol) in toluene (150 ml) was heated under reflux under N_2 for 18 h. The solvent was distilled off and the residue was subjected to flash chromatography, which gave (with ethyl acetate) the *pyridazinone* (**5b**) (0.50 g, 71%), m.p. 192—193 °C (from ethyl acetate) (Found: C, 65.1; H, 5.5; N, 10.9. $C_{14}H_{14}N_2O_3$ requires C, 65.2: H, 5.5; N, 10.85%); $\nu_{max.}$(KBr) 1 760 and 1 660 cm^{-1} (C=O); δ(400 MHz) 2.28 (3 H), 2.93—3.02 (1 H, m, 7a-H), 3.12 (1 H, dd, $J_{11'}$ 13.5 Hz, J_{17a} 10.2 Hz, 1-H), 3.26 (1 H, d, J_{4a7a} 7.7 Hz, 4a-H), 4.23 (1 H, dd, $J_{77'}$ 9.5 Hz, J_{77a} 2.5 Hz, 7-H), 4.50 (1 H, dd, $J_{7'7a}$ 6.2 Hz, 7′-H), 4.57 (1 H, dd, $J_{1'7a}$ 4.8 Hz, 1′-H), 7.36—7.41 (2 H, m), 7.43—7.49 (1 H, m), and 7.66—7.69 (2 H, m). The spectrum also showed small long-range couplings which were assigned as follows: $J_{1'4a}$ 1.2 Hz, J_{17} 0.3 Hz, and $J_{4a7'}$ 0.3 Hz; *m/z* 258 (M^+) and 105 (base).

4-*Methyl*-2-*phenyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one* (**5c**).—A solution of the azoalkene (**4c**) (1.0 g, 4.4 mmol) in toluene (150 ml) was heated under reflux under N_2 for 18 h. The solvent was distilled off and the residue was subjected to flash chromatography, which gave (with ether) the *pyridazinone* (**5c**) (0.31 g, 31%) as an oil (Found: *m/z* 230.1046. $C_{13}H_{14}N_2O_2$ requires 230.1055); $\nu_{max.}$(film) 1 760 cm^{-1} (C=O); δ(250 MHz) 2.23 (3 H), 2.86—2.92 (2 H, m, 7a-H and 1-H), 3.07 (1 H, d, J_{4a7a} 7.4 Hz, 4a-H), 3.66 (1 H, dd, $J_{11'}$ 16.8 Hz, $J_{1'7a}$ 9.3 Hz, 1′-H), 4.10 (1 H, dd, $J_{77'}$ 9.3 Hz, J_{77a} 2.3 Hz, 7-H), 4.36 (1 H, d, $J_{7'7a}$ 5.6 Hz, 7′-H), 6.92 (1 H, t, *J* 7.3 Hz), and 7.15—7.30 (4 H, m); *m/z* 230 (M^+), 205, and 84 (base).

2-(2,4-*Dinitrophenyl*)-4-*methyl*-1-*phenyl*-1,2,4a,7a-*tetrahydrofuran*[3,4-d]*pyridazin*-5(7H)-*one* (**10a**).—A solution of the 2,„4-dinitrophenylhydrazone (**8a**) (1.0 g, 2.3 mmol) in dichloromethane (100 ml) was stirred with sodium carbonate (3.0 g) for 24 h. The reaction mixture was filtered and the filtrate was evaporated to dryness to leave a yellow solid (0.91 g, 100%). Crystallisation gave the *pyridazinone* (**10a**), m.p. 120—123 °C (from dichloromethane–hexane) (Found: C, 57.3; H, 4.2; N, 13.9. $C_{19}H_{16}N_4O_6$ requires C, 57.6: H, 4.0; N, 14.1%); $\nu_{max.}$(KBr) 1 770 cm^{-1} (C=O); δ(250 MHz) 2.46 (3 H), 3.02 (1 H, d, J_{4a7a} 8.2 Hz, 4a-H), 3.48 (1 H, dddt, 7a-H), 4.39 (1 H, dd, $J_{77'}$ 9.8 Hz, J_{77a} 8.5 Hz, 7-H), 4.63 (1 H, dd, $J_{7'7a}$ 7.0 Hz, 7′-H), 4.90 (1 H, d, J_{17a} 3.5 Hz, 1-H), 6.78 (1 H, d, *J* 9.1 Hz), 7.16—7.20 (3 H, m), 7.35—7.40 (2 H, m), 8.09 (1 H, dd), and 8.54 (1 H, d, *J* 2.3 Hz); *m/z* 396 (M^+), 379, and 44 (base).

2-(2,4-*Dinitrophenyl*)-4,7-*dimethyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one* (**10b**).—A solution of the azoalkene (**9b**) (3.0 g, 8.9 mmol) in toluene (150 ml) was heated under reflux under N_2 for 3 h. The solvent was distilled off to leave a yellow solid. Flash chromatography of this gave (with dichloromethane–hexane) the *pyridazinone* (**10b**) (2.0 g, 67%), m.p. 203—205 °C (from dichloromethane) (Found: C, 50.4; H, 4.2; N, 16.9. $C_{14}H_{14}N_4O_6$ requires C, 50.3: H, 4.2; N, 16.8%); $\nu_{max.}$(KBr) 1 770 cm^{-1} (C=O); δ[250 MHz, $(CD_3)_2SO$] 1.71 (3 H, d, *J* 6.2 Hz, 7-Me), 2.12 (3 H), 3.01 (1 H, m, 7a-H), 3.53 (1 H, ddd, $J_{11'}$ 12.3 Hz, J_{17a} 8.2 Hz, 1-H), 3.75 (1 H, br d, J_{4a7a} 8.1 Hz, 4a-H), 4.10 (1 H, ddd, $J_{1'7a}$ 4.9 Hz, 1′-H), 4.63 (1 H, dq, J_{77a} 4.5 Hz, 7-H), 7.50 (1 H, d, *J* 9.2 Hz), 8.36 (1 H, dd), and 8.50 (1 H, d, *J* 2.6 Hz); *m/z* 334 (M^+, base) and 317.

2-(2,4-*Dinitrophenyl*)-4,4a-*dimethyl*-1-*phenyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one*(**10c**).—A solution of the 2,4-dinitrophenylhydrazone (**8c**) (0.15 g, 0.33 mmol) in dichloromethane (20 ml) was stirred with sodium carbonate (0.45 g) for 48 h. The reaction mixture was filtered and the filtrate was evaporated to dryness to leave a yellow solid (0.13 g, 100%). Crystallisation of this gave the *pyridazinone* (**10c**), m.p. 254—255 °C (from dichloromethane–light petroleum) (Found: C, 57.4; H, 4.3; N, 13.4. $C_{20}H_{18}N_4O_6$ requires C, 57.3: H, 4.4; N, 13.7%); $\nu_{max.}$(KBr) 1 770 cm^{-1} (C=O); δ(250 MHz) 0.90 (3 H), 2.01 (3 H), 3.30 (1 H, ddd, 7a-H), 4.30 (1 H, dd, $J_{77'}$ 9.9 Hz, J_{77a} 10.5 Hz, 7-H), 4.62 (1 H, dd, $J_{7'7a}$ 8.3 Hz, 7′-H), 5.17 (1 H, d, J_{17a} 2.1 Hz, 1-H), 6.75 (1 H, d, *J* 9.2 Hz), 7.11—7.15 (3 H, m), 7.37—7.41 (2 H, m), 8.13 (1 H, dd), and 8.54 (1 H, d, *J* 2.5 Hz); *m/z* 410 (M^+), 393, and 69 (base). Irradiation of the signal for 4a-Me caused n.O.e. enhancement of the signals at 2.01 (4-Me), 3.30 (7a-H), and 7.37—7.41 (*ortho* hydrogens of 1-Ph).

4a-*Chloro*-2-(2,4-*dinitrophenyl*)-4-*methyl*-1,2,4a,7a-*tetrahydrofuro*[3,4-d]*pyridazin*-5(7H)-*one* (**10d**).—A solution of the azoalkene (**9d**) (1.9 g, 5.4 mmol) in toluene (190 ml) was heated under reflux under N_2 for 24 h. The solvent was evaporated off and the residue was subjected to flash chromatography, which gave (with dichloromethane) the *pyridazinone* (**10d**) (1.15 g, 61%), m.p. 185 °C (decomp.) (from acetone) (Found: C, 43.95; H, 3.1;N, 15.5. $C_{13}H_{11}ClN_4O_6$ requires C, 44.0: H, 3.1; N, 15.8%); $\nu_{max.}$(KBr) 1 785 cm^{-1}; δ(250 MHz) 2.02 (3 H), 3.71 (1 H, m, 7a-H), 3.96 (1 H, dd, $J_{11'}$ 13.0 Hz, J_{17a} 5.5 Hz, 1-H), 4.07 (1 H, dd, $J_{1'7a}$ 4.0 Hz, 1′-H), 4.13 (1 H, dd, $J_{77'}$ 9.4 Hz, J_{77a} 8.1 Hz, 7-H), 4.68 (1 H, dd, $J_{7'7a}$ 7.9 Hz, 7′-H), 7.53 1 H, d, *J* 9.3 Hz), 8.43 (1 H, dd), and 8.59 (1 H, d, *J* 2.6 Hz); *m/z* 354 (M^+, base) and 336.

2-(2,4-*Dinitrophenyl*)-4-*methyl*-1,2,4a,6,7,7a-*hexahydropyrrolo*[3,4-d]*pyridazin*-5-*one* (**13**).—A solution of the 2,4-dinitrophenylhydrazone(**12**) (0.94 g, 2.64 mmol) in dichloromethane (100 ml) was stirred with sodium carbonate for 24 h to give the corresponding azoalkene, which was isolated (42%) as a red oil by flash chromatography. The azoalkene (0.35 g, 1.1 mmol) was heated in toluene (35 ml) under reflux under N_2 for 24 h. Flash chromatography gave (with dichloromethane) the *pyridazinone* (**13**) (0.22 g, 35%) as a yellow solid, m.p. 206—212 °C (from ethanol) (Found: C, 48.8; H, 4.1; N, 22.1. $C_{13}H_{13}N_5O_5$ requires

C, 48.9: H, 4.2; N, 21.9%); $\nu_{max.}$(KBr) 3 310 (NH) and 1 700 (C=O) cm^{-1}; δ(250 MHz) 2.39 (3 H), 3.33 (1 H, m, 7a-H), 3.48—3.57 (2 H, m, 1-H and 1′-H, $J_{11'}$ 11.6 Hz), 3.65 (1 H, d, J_{4a7a} 8.0 Hz, 4a-H), 3.87—3.97 (2 H, m, 7-H and 7′-H, $J_{77'}$ 11.3 Hz, J_{77a} 4.1 Hz, $J_{7'7a}$ 5.4 Hz), 7.48 (1 H, d, *J* 9.1 Hz), 7.94 (1 H, NH), 8.47 (1 H, dd), and 8.76 (1 H, *J* 2.3 Hz); *m/z* 310 (M^+, base) and 290.

5-(2,4-*Dinitrophenyl*)-3,3a,4,5,7,8-*hexahydrocyclopenta*[c]-*furo*[3,4-d]*pyridazin*-1(9H)-*one* (**17a**).—A solution of the azoalkene (**16a**) (0.63 g, 1.8 mmol) in toluene (60 ml) was heated under reflux under N_2 for 48 h. The solvent was distilled off. Flash chromatography of the residue gave (with ethyl acetate) the *pyridazinone* (**17a**) as a yellow solid (0.44 g, 70%), m.p. 214—216 °C (from dichloromethane–light petroleum) (Found: C, 51.9; H, 4.2; N, 15.9. $C_{15}H_{14}N_4O_6$ requires C, 52.0: H, 4.05; N, 16.2%); $\nu_{max.}$(KBr) 1 765 cm^{-1} (C=O); δ(250 MHz) 1.85—2.15 (2 H, m), 2.20—2.40 (1 H, m, 3a-H), 2.43—2.75 (2 H, m), 2.80—3.10 (2 H, m), 3.40 (1 H, dd, $J_{44'}$ 12.9 Hz, J_{3a4} 9.4 Hz, 4-H), 3.85 (1 H, dd, $J_{3a4'}$ 5.4 Hz, 4′-H), 4.45 (1 H, dd, $J_{33'}$ 9.4 Hz, J_{33a} 6.2 Hz, 9-H), 4.85 (1 H, dd, $J_{3'3a}$ 0.5 Hz, 3′-H), 7.48 (1 H, d, *J* 9.3 Hz), 8.38 (1 H, dd), and 8.52 (1 H, d, *J* 2.6 Hz); *m/z* 346 (M^+), 329, 312, and 41 (base).

5-*t-Butoxycarbonyl*-3,3a,4,5,7,8-*hexahydrocyclopenta*[c]-*furo*[3,4-d]*pyridazin*-1(9H)-*one* (**17b**).—A solution of the azoalkene (**16b**) (1.33 g, 4.80 mmol) in toluene (150 ml) was heated under reflux under N_2 for 8 h. The solvent was distilled off. Flash chromatography of the residue gave (with dichloromethane–ethyl acetate) the *pyridazinone* (**17b**) as a pale yellow solid (0.98 g, 74), m.p. 197—199 °C (from ethyl acetate) (Found: C, 60.0; H, 7.2; N, 9.95. $C_{14}H_{20}N_2O_4$ requires C, 60.0: H, 7.2; N, 10.0%); $\nu_{max.}$(KBr) 1 770 and 1 703 cm^{-1} (C=O); δ(250 MHz, CF_3CO_2H) 1.55 (9 H), 1.95—2.25 (2 H, m), 2.30—2.65 (2 H, m), 2.70—2.93 (2 H, m), 2.90—3.10 (1 H, m, 3a-H), 3.22 (1 H, dd, $J_{44'}$ 13.3 Hz, J_{3a4} 7.8 Hz, 4-H), 3.56 (1 H, dd, $J_{3a4'}$ 6.5 Hz, 4′-H), 4.37 (1 H, dd, $J_{33'}$ 10.0 Hz, J_{33a} 6.7 Hz, 3′-H), and 4.80 (1 H, $J_{3'3a}$ 0.5 Hz, 3′-H).

5-*Phenyl*-3,3a,4,5,7,8-*hexahydrocyclopenta*[c]*furo*[3,4-d]*pyridazin*-1(9H)-*one* (**17c**).—A solution of the azoalkene (**16c**) (0.77 g, 3.0 mmol) in toluene (80 ml) was heated under reflux under N_2 for 5 days. The solvent was distilled off. Flash chromatography of the residue gave (with dichloromethane) the *pyridazinone* (**17c**) as a colourless solid (0.60 g, 79%), m.p. 105—106 °C (from dichloromethane–light petroleum) (Found: C, 70.1; H, 6.3; N, 10.9. $C_{15}H_{16}N_2O_2$ requires C, 70.3: H, 6.25; N, 10.9%); $\nu_{max.}$(KBr) 1 760 cm^{-1} (C=O); δ(250 MHz) 1.65—1.85 (1 H, m), 1.86—2.13 (1 H, m), 2.14—2.43 (2 H, m), 2.45—2.67 (2 H, m), 2.90—3.02 (2 H, m, 1-H and 3a-H), 3.65 (1 H, dd, $J_{44'}$ 12.4 Hz, J_{3a4} 5.3 Hz, 4′-H), 4.14 (1 H, dd, $J_{33'}$ 9.3 Hz, J_{33a} 6.0 Hz, 3-H), 4.50 (1 H, dd, $J_{3'3a}$ 0.5 Hz, 3′-H), 6.88—6.91 (1 H, m), and 7.17—7.30 (4 H, m); *m/z* 256 (M^+), 120, and 77 (base).

5-(2,4-*Dinitrophenyl*)-3,3a,4,5,7,8,9,10-*octahydrofuro*[3,4-d]*cinnolin*-1-*one* (**21a**).—A solution of the azoalkene (**20a**) (1.01 g, 2.80 mmol) in toluene (100 ml) was heated under reflux under N_2 for 10 days. The solvent was distilled off. Flash chromatography of the residue gave (with dichloromethane) the *pyridazinone* (**21a**) as an orange solid (0.60 g, 60%), m.p. 218—222 °C (from dichloromethane–light petroleum) (Found: C, 53.3; H, 4.45; N, 15.7. $C_{16}H_{16}N_4O_6$ requires C, 53.3: H, 4.5; N, 15.55%); $\nu_{max.}$(KBr) 1 760 cm^{-1} (C=O); δ(250 MHz) 1.66—1.96 (4 H, m), 2.11—2.21 (2 H, m), 2.52—2.63 (2 H, m), 2.98—3.10 (1 H, m, 3a-H), 3.53 (1 H, dd, $J_{44'}$ 12.5 Hz, J_{3a4} 10.1 Hz, 4-H), 4.12 (1 H, dd, $J_{3a4'}$ 4.6 Hz, 4′-H), 4.44 (1 H, $J_{33'}$ 10.2 Hz, J_{33a} 6.3 Hz, 3-H), 4.80 (1 H, dd, $J_{3'3a}$ 0.5 Hz, 3′-H), 7.53 (1 H, d, *J* 9.1 Hz), 8.47 (1 H, dd), and 8.73 (1 H, d, *J* 2.3 Hz); *m/z* 360 (M^+), 325, and 41 (base).

5-*t-Butoxycarbonyl*-3,3a,4,5,7,8,9,10-*octahydrofuro*[3,4-d]-*cinnolin*-1-*one* (**21b**).—A solution of the azoalkene (**20b**) (0.89 g, 3.02 mmol) in toluene (90 ml) was heated under reflux under N_2 for 5 days. The solvent was distilled off. Flash chromatography of the residue gave (with ethyl acetate) the *pyridazinone* (**21b**) (0.57 g, 65%), m.p. 155—158 °C (from dichloromethane–light petroleum) (Found: C, 61.4; H, 7.6; N, 9.6. $C_{15}H_{22}N_2O_4$ requires C, 61.2: H, 7.5; N, 9.5%); $\nu_{max.}$(KBr) 1 765 and 1 695 cm^{-1} (C=O); δ(250 MHz, $CDCl_3$–CF_3CO_2H) 1.61 (9 H), 1.70—1.90 (4 H, m), 2.20—2.60 (2 H, m), 2.78—2.83 (2 H, m), 2.95—3.00 (1 H, m, 3a-H), 3.24 (1 H, dd, $J_{44'}$ 13.0 Hz, J_{3a4} 6.1 Hz, 4-H), 3.74 (1 H, dd, $J_{3a4'}$ 5.0 Hz, 4′-H), 4.40 (1 H, $J_{33'}$ 10.5 Hz, J_{33a} 6.1 Hz, 3-H), and 4.76 (1 H, dd, $J_{3'3a}$ 0.5 Hz, 3′-H); *m/z* 294 (M^+), 194, and 44 (base).

5-*Phenyl*-3,3a,4,5,7,8,9,10-*octahydrofuro*[3,4-d]*cinnolin*-1-*one* (**21c**).—A solution of the azoalkene (**20c**) (1.04 g, 3.85 mmol) in xylene (100 ml) was heated under reflux under N_2 for 8 days. The solvent was distilled off. Flash chromatography of the residue gave (with dichloromethane) the *pyridazinone* (**21c**) as a yellow solid (0.62 g, 60%), m.p. 172—173 °C (from ether) (Found: C, 71.1; H, 6.7; N, 10.3. $C_{16}H_{18}N_2O_2$ requires C, 71.1: H, 6.7; N, 10.4%); $\nu_{max.}$(KBr) 1 760 cm^{-1} (C=O); δ(250 MHz) 1.23—1.73 (4 H, m), 2.01—2.18 (2 H, m), 2.23—2.57 (2 H, m), 2.87—3.00 (1 H, m, 3a-H), 3.11 (1 H, dd, $J_{44'}$ 12.2 Hz, J_{3a4} 8.9 Hz, 4-H), 3.71 (1 H, dd, $J_{3a4'}$ 4.6 Hz, 4′-H), 4.14 (1 H, $J_{33'}$ 9.4 Hz, J_{33a} 4.0 Hz, 3-H), 4.47 (1 H, dd, $J_{3'3a}$ 0.5 Hz, 3′-H), 6.91—6.97 (1 H, m), and 7.19—7.33 (4 H, m); *m/z* 270 (M^+) and 219 (base).

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