Addition and Cycloaddition Reactions of β-Chloroazo-olefins[1]

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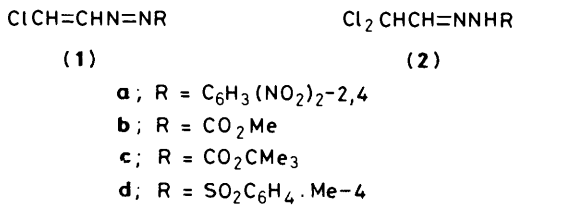
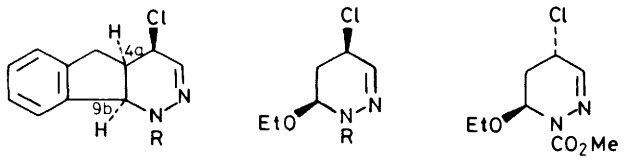
2-Chloro-1-(2,4-dinitrophenylazo)ethene (**1a**) has been isolated, and the corresponding alkoxycarbonylazo compounds (**1b**) and (**1c**) have been generated in solution, as the first examples of azo-olefins bearing single β-halogeno substituents. The compounds (**1a**) and (**1b**) undergo [4 + 2] cycloaddition to indene and to ethyl vinyl ether with high *endo* stereoselectivity. Furan and cyclopentadiene give the cycloadducts (**6**) and (**7**), respectively, with (**1a**). Nucleophilic addition–elimination reactions are observed with piperidine, indole, thiophenol, and carbanions. In most of these reactions the primary products are subject to further nucleophilic attack: thus, the hydrazones (**11**) formed by addition of carbanions are converted into aminopyrroles (**12**) by further reaction with the carbanions and dehydration.

β-Chloroazo-olefins of general structure (**1**) have not previously been prepared. Chattaway and Farinholt investigated reactions of dichloroacetaldehyde with arylhydrazines and observed transient colours in solution which they ascribed to azo-olefins.[2] We have investigated their preparation and properties, particularly their addition and cycloaddition reactions. The corresponding nitroso-olefin, 2-chloronitrosoethylene, has been generated as a transient intermediate[3] and has been shown to undergo addition–elimination reactions; it also acts as a four π-electron component in hetero-Diels-Alder reactions,[4] like many other nitroso-olefins.[5] In contrast, 2,2-dichloronitroso-ethylene acts as a two π-electron component (through the nitroso group) in cycloaddition reactions with conjugated dienes. As there is usually a broad similarity in the chemistry of nitroso- and azo-olefins we wished to establish whether this extended to the β-chloro derivatives. ββ-Dichloroazo-olefins undergo nucleophilic addition–elimination reactions readily[6] but no cycloaddition reactions of these compounds have so far been achieved.



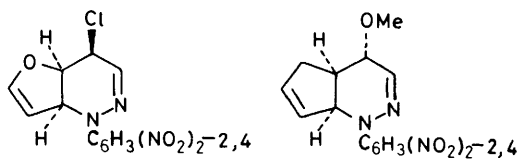
(**1**) (**2**)

a; R = $C_6H_3(NO_2)_2$-2,4
b; R = CO_2Me
c; R = CO_2CMe_3
d; R = $SO_2C_6H_4$·Me-4

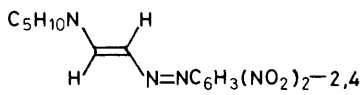


(**3**) (**4**) (**5**)

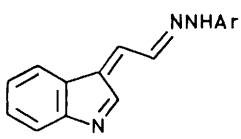
a; R = $C_6H_3(NO_2)_2$-2,4
b; R = CO_2Me



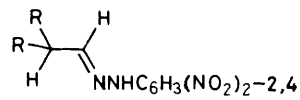
(**6**) (**7**)



(**8**)



(**10**)



(**9**) **a**; R = PhS
b; R = Indol-3-yl

Preparation of the Azo-olefins.—Dichloroacetaldehyde, prepared by the reduction of chloral hydrate, was converted into the known[7] 2,4-dinitrophenylhydrazone (**2a**). This derivative can also be prepared from the commercially available diethyl acetal of dichloroacetaldehyde. The alkoxycarbonylhydrazones (**2b**) and (**2c**), which are new compounds, were prepared by the same method as that reported for the preparation of the toluene-*p*-sulphonylhydrazone (**2d**).[8]

The azo-olefins (**1a**—**c**) were generated from the hydrazones by reaction with anhydrous sodium carbonate suspended in dichloromethane. The 2,4-dinitrophenylazo-olefin (**1a**) was isolated as a red crystalline solid. The ^1H n.m.r. spectrum of the compound in $CDCl_3$ indicates that it is a 7:3 mixture of (*E*)- and (*Z*)-isomers. Azo-olefin (**1b**) was isolated as an orange solid which proved to be unstable, and it was not fully characterised. The compound is, however, long-lived in solution. N.m.r. and i.r. solution spectra were obtained for both the azo-olefins (**1b**) and (**1c**); in each case n.m.r. showed the presence of only a single isomer, which was identified as the (*E*)-isomer on the basis of the coupling constant (11.9 Hz) for the vinylic hydrogens.

Cycloaddition Reactions.—In common with many other azo-olefins,[9] but in contrast to the ββ-dichloroazo-olefins, compounds (**1a**) and (**1b**) were found to participate as the four π-electron components in Diels–Alder reactions with electron-rich dienophiles. The azo-olefin (**1a**) reacted slowly with indene

at room temperature to give, in high yield, a 1:1 adduct as a single stereoisomer. This was assigned structure (**3a**), with an all-*cis* arrangement of substituents at C-4, C-4a, and C-9b, on the basis of the vicinal coupling constants in the n.m.r. spectrum. The coupling constants $J_{4,4a}$ = 6.7 Hz and $J_{4a,9b}$ = 7.2 Hz are consistent with a structure in which 4-H and 9b-H occupy pseudo-equatorial positions and 4a-H a pseudo-axial position. The azo-olefin (**1b**) gave an an analogous adduct (**3b**) with indene; again, only one stereoisomer was detected. Ethyl vinyl ether also formed 1:1 adducts with each of these azo-olefins. That from compound (**1a**) was a single stereoisomer, which was assigned structure (**4a**). The corresponding adduct (**4b**) was isolated as the major product of the reaction of azo-olefin (**1b**) with ethyl vinyl ether; an isomer, which was assigned structure (**5**), was also isolated. The tetrahydropyridazines (**4b**) and (**5**) were clearly distinguishable by n.m.r.; in particular, 4-H in (**4b**) (δ 4.33) shows only weak vicinal coupling whereas 4-H in (**5**) (δ 4.64) is strongly coupled (*J* 12.2 Hz) to one of the adjacent hydrogens at C-5. In both isomers 6-H shows only weak vicinal coupling, indicating that the 6-ethoxy groups occupy pseudo-axial positions: the anomeric effect is observed in these, as in related,[10] tetrahydropyridazines. In the compounds (**4**) the chloro substituents at C-4 are *cis* to the ethoxy groups at C-6, and so also occupy pseudo-axial positions. The adduct (**4b**) was found to isomerise to compound (**5**) when stored for several weeks at −50 °C; thus, (**5**) may be a secondary product of the reaction.

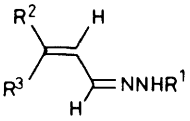
Furan reacted with the azo-olefin (**1a**) to give a cyclo-adduct which was assigned the structure (**6**). Cyclopentadiene also reacted with this azo-olefin but the primary reaction product could not be isolated by chromatography; instead, a displacement product (**7**) was obtained after elution of the chromatography column with methanol.

In these reactions the azo-olefins (**1a**) and (**1b**) act as heterodienes. Moreover, in those adducts for which the stereochemistry can be deduced from the n.m.r. spectra, the relative positions of the substituents are consistent with *endo* addition to the (*E*)-azo-olefins as the primary reaction. This observation applies to the azo-olefin (**1a**) which, as described earlier, exists as an (*E*)/(*Z*) mixture in solution. It seems likely that these isomers can interconvert easily, and that addition takes places preferentially to the (*E*)-isomer. The preference for *endo* transition states in these reactions is consistent with previous studies of azo-olefin additions.[10,11]

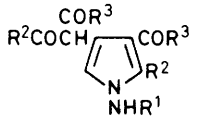
Addition–Elimination Reactions with Nucleophiles.—The azo-olefin (**1a**) reacted readily with a range of nucleophiles. Piperidine gave the addition–elimination product (**8**), analogous to those formed from ββ-dichloroazo-olefins and secondary amines.[6] Although both thiophenol and indole also reacted with (**1a**) in the presence of sodium carbonate, simple addition–elimination products were not detected; instead, the products (**9**), each incorporating two moles of the nucleophile, were isolated in moderate yield. The reasons for further addition of thiophenol in such reactions have been discussed earlier;[6] in the case of reaction with indole, an intermediate addition–elimination product in the tautomeric form (**10**) would be highly susceptible to nucleophilic attack.

The azo-olefins (**1a**) and (**1b**) reacted readily with activated methylene compounds in the presence of base to give the hydrazones (**11**). These are the products to be expected from addition–elimination reactions of the carbanions, followed by tautomerisation. Further attack of the carbanions on these hydrazones was observed in several cases. Pyrroles (**12**) were isolated, these being the products of Michael addition of the carbanions to the hydrazones followed by cyclodehydration of the adducts. Evidence for this sequence was provided by the reaction of the hydrazone (**11b**) with pentane-2,4-dione, which gave the pyrrole (**12b**). This pyrrole was also formed directly by the reaction of the azo-olefin (**1b**) with an excess of pentane-2,4-dione in the presence of sodium carbonate. The azo-olefin (**1a**) reacted with dimedone (2 mol) to give the Michael adduct (**13**), which was cyclised to the pyrrole (**12d**) on treatment with acid. Ethyl acetoacetate reacted in a similar manner with (**1a**) but the Michael adduct was formulated as the cyclic tautomer (**14**) (as a mixture of diastereoisomers) on the basis of its n.m.r. spectrum. This compound was also converted into a pyrrole, compound (**12c**), by reaction with acid.

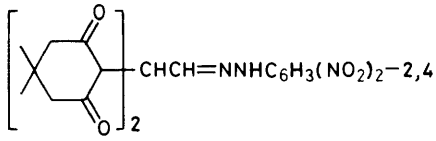
Conjugate nucleophilic addition to unsaturated hydrazones of type (**11**) should, in principle, provide a more general route to pyrroles. Severin and his co-workers have described related reactions in which pyrroles (**16**) are formed by reduction of the hydrazones (**15**).[12] However, preliminary experiments, in which carbanions derived from other activated methylene compounds were added to the hydrazones (**11**) were unsuccessful in this respect: although the additions took place, mixtures of products resulted and pyrroles were not isolated in useful yield.



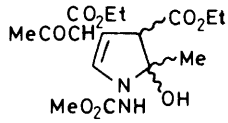
(**11**) **a**; R^1 = $C_6H_3(NO_2)_2$-2,4, R^2 = R^3 = Ac
b; R^1 = CO_2Me, R^2 = R^3 = Ac
c; R^1 = CO_2Me, R^2 = R^3 = Bz
d; R^1 = CO_2Me, R^2 = R^3 = CO_2Et
e; R^1 = CO_2Me, R^2 = R^3 = CN
f; R^1 = CO_2Me, R^2 = NO_2, R^3 = CO_2Et
g; R^1 = CO_2Me, R^2R^3 = CO_2CMe_2OCO



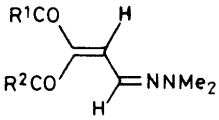
(**12**) **a**; R^1 = $C_6H_3(NO_2)_2$-2,4, R^2 = R^3 = Me
b; R^1 = CO_2Me, R^2 = R^3 = Me
c; R^1 = $C_6H_3(NO_2)_2$-2,4, R^2 = Me, R^3 = OEt
d; R^1 = $C_6H_3(NO_2)_2$-2,4, R^1R^2 = $CH_2CMe_2CH_2$



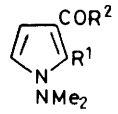
(**13**)



(**14**)



(**15**)



(**16**)

Experimental

I.r. spectra were recorded as KBr discs. ^{1}H N.m.r. spectra were recorded at 220 MHz in $CDCl_3$ on a Perkin-Elmer R34 instrument, and ^{13}C n.m.r. spectra at 25.2 MHz on a Varian XL100 spectrometer, except where indicated otherwise. Electron impact mass spectra were obtained on AEI MS12 and MS902 instruments. Melting points are uncorrected. Ether refers to diethyl ether. Light petroleum refers to that fraction boiling in the range (60—80 °C).

Dichloroacetaldehyde Methoxycarbonylhydrazone (**2b**).—Freshly distilled dichloroacetaldehyde (5.0 g, 44.3 mmol) was added to a stirred solution of methoxycarbonylhydrazine (3.62 g, 40.2 mmol) in propanoic acid (30 cm^3) at room temperature. After 1 h the reaction mixture was cooled to 0 °C and left at this temperature for 6 h. The solid which was filtered off, washed, dried, and crystallised was the *hydrazone* (**2a**) (4.9 g, 66%), m.p. 180—181 °C (from ethyl acetate–hexane) (Found: C, 26.2; H, 3.1; N, 14.8. $C_4H_6Cl_2N_2O_2$ requires C, 25.9; H, 3.2; N, 15.1%); $\nu_{max.}$ 3 230 (NH) and 1 710 cm^{-1} (CO); δ[$(CD_3)_2CO$] 3.77 (3 H), 6.61 (1 H, d, *J* 8.0 Hz), 7.67 (1 H, d, *J* 8.0 Hz) and 10.22 (1 H); *m/z* 188, 186, and 184 (M^+).

Dichloroacetaldehyde t-Butoxycarbonylhydrazone (**2c**).—Dichloroacetaldehyde (2.0 g, 17.7 mmol) and t-butoxycarbonylhydrazine (2.33 g, 17.7 mmol) similarly gave the *hydrazone* (**2c**) (2.85 g, 71%), m.p. 115 °C (decomp.) (from chloroform–hexane) (Found: C, 36.8; H, 5.3; N, 12.1. $C_7H_{12}Cl_2N_2O_2$ requires C, 37.0; H, 5.3; N, 12.3%); $\nu_{max.}$ 3 260 (NH) and 1 710 cm^{-1} (CO); δ 1.50 (9 H), 6.29 (1 H, d, *J* 8.0 Hz), 7.45 (1 H, d, *J* 8.0 Hz), and 8.72 (1 H); *m/z* (by chemical ionisation) 231, 229, and 227 ($M^+ + 1$), 171, and 57 (base).

2-*Chloro*-1-(2,4-*dinitrophenylazo*)*ethene* (**1a**).—Dichloroacetaldehyde 2,4-dinitrophenylhydrazone[7] (0.40 g, 1.37 mmol) was stirred with anhydrous sodium carbonate (0.6 g, 5.66 mmol) in dichloromethane (50 cm^3) for 24 h at room temperature. Evaporation of the filtrate gave a red solid which was crystallised to give the *azo-olefin* (**1a**) (0.255 g, 73%), m.p. 73—74 °C (from dichloromethane–light petroleum) (Found: C, 37.5; H, 1.9; N, 22.1. $C_8H_5ClN_4O_4$ requires C, 37.4; H, 1.9; N, 21.8%); $\nu_{max.}$ 1 600, 1 580, 1 540, 1 515, and 1 340 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 327 nm (ε 18 700); δ[(*Z*)-isomer] 7.22 and 7.61 (each 0.3 H, d, *J* 5.5 Hz) and [(*E*)-isomer] 7.72 and 7.79 (each 0.7 H, d, *J* 12.0 Hz); 7.60—7.65 (1 H, m), 8.48—8.58 (1 H, m), and 8.75—8.79 (1 H, m); *m/z* 258 and 256 (M^+).

1-*Chloro*-2-(*methoxycarbonylazo*)*ethene* (**1b**).—The hydrazone (**2b**) (0.50 g, 2.7 mmol) in tetrachloromethane (50 cm^3) was stirred with sodium carbonate (1.0 g) for 24 h. The solution was evaporated to small volume and the azo-olefin was identified from solution spectra: $\nu_{max.}$ 1 770 (CO), 1 600, and 1 480 cm^{-1}; $\lambda_{max.}$ 412 nm; δ (60 MHz, CCl_4) 3.98 (3 H), 7.46 (1 H, d, *J* 11.9 Hz), and 7.80 (1 H, d, *J* 11.9 Hz).

2-(t-*Butoxycarbonylazo*)-1-*chloroethene* (**1c**).—By the method described for compound (**1b**) the azo-olefin (**1c**) was obtained in tetrachloromethane solution from the hydrazone (**2c**) (0.50 g, 2.2 mmol); $\nu_{max.}$ 1 765 (CO), 1 600, and 1 480 cm^{-1}; δ (60 MHz, CCl_4) 1.58 (9 H), 7.38 (1 H, d, *J* 11.9 Hz), and 7.68 (1 H, d, *J* 11.9 Hz).

4-*Chloro*-1-(2,4-*dinitrophenyl*)-4,4a,5,9b-*tetrahydro*-1H-*indeno*[1,2-c]*pyridazine* (**3a**).—A solution of the azo-olefin (**1a**) (0.30 g, 1.17 mmol) and indene (0.40 g, 5.55 mmol) in dichloromethane (50 cm^3) was kept at room temperature until the azo-olefin was no longer detectable (6 days). Column chromatography (silica; ether–light petroleum 1:2) gave the *pyridazine* (**3a**) (0.41 g, 94%), m.p. 152—154 °C (from chloroform–hexane) (Found: C, 54.7; H, 3.5; N, 15.2. $C_{17}H_{13}ClN_4O_4$ requires C, 54.8; H, 3.5; N, 15.0%); $\nu_{max.}$ 1 595, 1 520, and 1 505 cm^{-1}; δ 3.27 (2 H, m, 5-H), 3.51 (1 H, m, 4a-H), 4.78 (1 H, dd, *J* 6.7 and 2.5 Hz, 4-H), 5.48 (1 H, d, *J* 7.2 Hz, 9b-H), 6.99—7.10 (3 H, m, 3-H and 2 Ar-H), 7.26 (2 H, m), 7.49 (1 H, d), 8.32 (1 H, dd), and 8.55 (1 H, d); decoupling experiments established $J_{3,4}$ 2.5 Hz, $J_{4,4a}$ 6.7 Hz, and $J_{4a,9b}$ 7.2 Hz; *m/z* 374 and 372 (M^+).

Methyl 4-*Chloro*-4,4a,5,9b-*tetrahydro*-1H-*indeno*[1,2-c]*pyridazine*-1-*carboxylate* (**3b**).—To a solution of the hydrazone (**2b**) (0.50 g, 2.7 mmol) and indene (1.0 cm^3, 8.6 mmol) in dichloromethane (50 cm^3) was added sodium carbonate (1.0 g) and the mixture was stirred for 48 h. The azo-olefin (**1b**) was still detectable (t.l.c.). The reaction mixture was then heated under reflux for 24 h, cooled, and filtered. Layer chromatography of the filtrate gave the *pyridazine* (**3b**) (0.35 g, 49%), m.p. 136—137 °C (from dichloromethane–hexane) (Found: C, 59.0; H, 5.1; N, 10.4. $C_{13}H_{13}ClN_2O_2$ requires C, 59.0; H, 5.1; N, 10.6%); $\nu_{max.}$ 1 700 and 1 610 cm^{-1} (CO); δ 3.14 (2 H, m, 5-H), 3.44 (1 H, m, 4a-H), 3.87 (3 H), 4.63 (1 H, dd, *J* 5.8 and 2.2 Hz, 4-H), 5.60 (1 H, d, *J* 8.3 Hz, 9b-H), 7.15—7.30 (4 H, m, 3-H and 3 Ar-H), and 7.57 (1 H, m); decoupling established $J_{3,4}$ 2.2 Hz, $J_{4,4a}$ 5.8 Hz, and $J_{4a,9b}$ 8.3 Hz; *m/z* 266 and 264 (M^+).

4-*Chloro*-1-(2,4-*dinitrophenyl*)-6-*ethoxy*-1,4,5,6-*tetrahydropyridazine* (**4a**).—The azo-olefin (**1a**) (0.50 g, 1.95 mmol), toluene (10 cm^3), and ethyl vinyl ether (3 cm^3) were heated in a sealed tube at 50 °C for 24 h. Column chromatography (silica) and elution with ether gave the *pyridazine* (**4a**) (0.49 g, 77%), m.p. 110 °C (decomp.) (from ether–hexane) (Found: C, 43.6; H, 3.9; N, 16.9. $C_{12}H_{13}ClN_4O_5$ requires C, 43.8; H, 4.0; N, 17.0%); $\nu_{max.}$ 1 600, 1 535, 1 510, and 1 333 cm^{-1}; δ 1.25 (3 H, t), 2.49 (1 H, ddd, *J* 15.5, 6.8, and 2.8 Hz, 5-H), 2.87 (1 H, d, *J* 15.5 Hz, showing further small coupling, 5′-H), 3.62 (2 H, m), 4.41 (1 H, d, *J* 6.8 Hz, showing further coupling, 4-H), 5.23 (1 H, *ca.* t, 6-H), 7.08 (1 H, m, 3-H), 7.46 (1 H, d), 8.36 (1 H, dd), and 8.57 (1 H, d); decoupling established $J_{4,5}$ = 6.8 Hz, $J_{4,5'}$ = *ca.* 1 Hz, $J_{5,5'}$ = 15.5 Hz, $J_{5,6}$ = 2.8 Hz, and $J_{5',6}$ = *ca.* 2.7 Hz; *m/z* 293 (M^+ − 35) and 202 (base).

Methyl 4α-*Chloro*-6α-*ethoxy*-1,4,5,6-*tetrahydropyridazine*-1-*carboxylate* (**4b**) *and its* 4β-*Isomer* (**5**).—The hydrazone (**2b**) (0.50 g, 2.7 mmol) and ethyl vinyl ether (1 cm^3) were stirred in dichloromethane (50 cm^3) with sodium carbonate (1 g) for 48 h. Layer chromatography (silica) gave, with dichloromethane as eluant, the *pyridazine* (**4b**) (0.30 g, 51%) as an oil (Found: M^+, 220.06146. $C_8H_{13}ClN_2O_3$ requires M^+, 220.061 04); δ 1.03 (3 H, t), 2.18 (1 H, ddd, *J* 15.6, 7.2, and 3.3 Hz, 5-H), 2.54 (1 H, d, *J* 15.6 Hz, showing further coupling, 5′-H), 3.41 (2 H, m), 3.74 (3 H), 4.33 (1 H, dd, *J* 7.2 and 3.0 Hz, 4-H), 5.61 (1 H, *ca.* t, *J ca.* 3 Hz, 6-H), and 6.99 (1 H, s, br, 3-H); decoupling gave $J_{4,5}$ = 7.2 Hz, $J_{4,5'}$ = 3.0 Hz, $J_{5,5'}$ = 15.6 Hz, $J_{5,6}$ = 3.3 Hz, and $J_{5',6}$ = *ca.* 3 Hz. A second band from the plate was extracted and gave the *pyridazine* (**5**) as an oil (Found: M^+, 220.061 46); δ 1.14 (3 H, t), 1.97 (1 H, ddd, *J* 12.5, 12.2, and 2.3 Hz, 5-H), 2.54 (1 H, m, 5′-H), 3.60 (2 H, q), 3.87 (3 H), 4.64 (1 H, dd, *J* 12.2 and 7.2 Hz, showing further coupling, 4-H), 5.64 (1 H, *ca.* t, *J ca.* 2 Hz, 6-H), and 6.95 (1 H, s, br, 3-H); decoupling gave $J_{4,5}$ = 12.2 Hz, $J_{4,5'}$ = 7.2 Hz, $J_{5,5'}$ = 12.5 Hz, $J_{5,6}$ = 2.3 Hz, and $J_{5',6}$ = *ca.* 2 Hz. Over a period of several weeks at −50 °C, the pyridazine (**4b**) isomerised to (**5**).

4-*Chloro*-1-(2,4-*dinitrophenyl*)-1,4,4a,7a-*tetrahydrofuro*[3,2-c]*pyridazine* (**6**).—The azo-olefin (**1a**) (0.30 g, 1.17 mmol), furan (5 cm^3), and dichloromethane (50 cm^3) were mixed and the solution set aside until the azo-olefin was no longer detectable

(18 days). Column chromatography (silica) and elution with ether–hexane (2:1) gave the *pyridazine* (**6**) (0.285 g, 75%), m.p. 162—163 °C (from dichloromethane–hexane) (Found: C, 44.3; H, 2.9; N, 17.2. $C_{12}H_9ClN_4O_5$ requires C, 44.4; H, 2.8; N, 17.2%); $\nu_{max.}$ 1 600, 1 533, 1 504, and 1 335 cm^{-1}; δ[$(CD_3)_2CO$] 4.90 (1 H, m, 4-H), 5.43 (1 H, m, 7-H), 5.61 (1 H, d, *J* 10.0 Hz, showing further coupling, 4a-H), 5.74 (1 H, d, *J* 10.0 Hz, showing further coupling, 7a-H), 6.71 (1 H, m, 6-H), 7.52 (1 H, m, 3-H), 7.67 (1 H, d), 8.43 (1 H, dd), and 8.54 (1 H, d); $J_{3,4}$ = *ca.* 1.5 Hz, $J_{4,4a}$ = *ca.* 2 Hz, and $J_{4a,7a}$ = 10.0 Hz; *m/z* 326 and 324 (M^+).

1-(2,4-*Dinitrophenyl*)-4-*methoxy*-4,4a,5,7a-*tetrahydro*-1H-*cylcopenta*[c]*pyridazine* (**7**).—A solution of the azo-olefin (**1a**) (0.30 g, 1.17 mmol) and cyclopentadiene (5 cm^3) in dichloromethane (50 cm^3) was kept at 20 °C for 20 h. Layer chromatography (silica) and development with ether–hexane (3:1) gave one major product which required elution with methanol to remove it from the support. This gave a solid which was identified as the *pyridazine* (**7**) (0.06 g, 16%), m.p. 162—165 °C (from dichloromethane–hexane) (Found: C, 52.9; H, 4.5; N, 17.5. $C_{14}H_{14}N_4O_5$ requires C, 52.8; H, 4.4; N, 17.6%); $\nu_{max.}$ 1 600, 1 535, and 1 330 cm^{-1}; δ 2.50—2.85 (3 H, m, 4a-H and 5-H), 3.40 (1 H, dd, *J* 10.0 and 2.0 Hz, 4-H), 3.54 (3 H), 5.00 (1 H, d, br, *J* 7.0 Hz, 7a-H), 5.89 (1 H, m), 6.14 (1 H, m), 7.21 (1 H, d), 7.26 (1 H, d, *J* 2.0 Hz, 3-H), 8.31 (1 H, dd), and 8.49 (1 H, d); *m/z* 318 (M^+).

1-[2-(2,4-*Dinitrophenylazo*)*ethenyl*]*piperidine* (**8**).—A solution of the azo-olefin (**1a**) (0.40 g, 1.55 mmol) in dichloromethane (50 cm^3) was stirred and piperidine (5 cm^3) was added dropwise. The solution was evaporated after 0.5 h to give the *azo-olefin* (**8**) (0.43 g, 91%), m.p. 153—154 °C (from dichloromethane–hexane) (Found: C, 51.2; H, 5.1; N, 23.3. $C_{13}H_{15}N_5O_4$ requires C, 51.2; H, 4.9; N, 23.0%); $\nu_{max.}$ 1 615, 1 585, and 1 310 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 326 (ε 6 200) and 488 nm (50 000); δ 1.77 (6 H), 3.55 (4 H), 7.55 (1 H, d, *J* 10.6 Hz), 7.65 (1 H, d, *J* 10.6 Hz), 7.78 (1 H, d), 8.26 (1 H, dd), and 8.50 (1 H, d); *m/z* 305 (M^+).

2,2-*Bisphenylthioacetaldehyde* 2,4-*Dinitrophenylhydrazone* (**9a**).—A solution of the azo-olefin (**1a**) (0.30 g, 1.17 mmol) and thiophenol (1 cm^3) in dichloromethane (50 cm^3) was stirred with anhydrous sodium carbonate (0.75 g) for 24 h and gave the dinitrophenylhydrazone (**9a**) (0.25 g, 49%), m.p. 138—140 °C (from dichloromethane–hexane) (lit.,[6] 138—139 °C).

2,2-*Di-indol*-3-*ylacetaldehyde* 2,4-*Dinitrophenylhydrazone* (**9b**).—The hydrazone (**2a**) (0.50 g, 1.7 mmol), indole (0.20 g, 1.7 mmol), and anhydrous sodium carbonate (1 g) were stirred in dichloromethane (50 cm^3) for 24 h. The filtrate gave, by layer chromatography (silica) and development with ether–hexane (4:1), the 2,4-*dinitrophenylhydrazone* (**9b**) [0.15 g, 39% based on the hydrazone (**2a**), yield not increased by the use of an excess of indole], m.p. 213—214 °C (from ethyl acetate–hexane) (Found: C, 63.3; H, 4.2; N, 18.2. $C_{24}H_{18}N_6O_4$ requires C, 63.4; H, 4.0; N, 18.5%); $\nu_{max.}$ 3 400 (NH), 3 270 (NH), 1 615, 1 590, and 1 325 cm^{-1}; δ[$(CD_3)_2CO$] 5.59 (1 H, d, *J* 7.3 Hz, 2-H), 6.97 (2 H, m), 7.09 (2 H, m), 7.25 (2 H, m), 7.39 (2 H, m), 7.62 (2 H, m), 8.06 (1 H, d), 8.32 (1 H, dd), 8.42 (1 H, d, *J* 7.3 Hz, 1-H), 8.92 (1 H, d), 10.17 (2 H), and 11.28 (1 H).

3-*Acetylpent*-2-*ene*-1,4-*dione* 1-(2,4-*Dinitrophenylhydrazone*) (**11a**).—The azo-olefin (**1a**) (0.50 g, 1.95 mmol) and pentane-2,4-dione (0.195 g, 1.95 mmol) in dichloromethane (50 cm^3) were stirred for 4 h with anhydrous sodium carbonate (1 g). The filtrate gave, by column chromatography (silica) and elution with ether–hexane (1:1), the azo-olefin (**1a**) (0.324 g) and the *hydrazone* (**11a**) (0.144 g, 65% based on azo-olefin consumed), m.p. 170 °C (from chloroform) (Found: C, 48.9; H, 3.6; N, 17.3. $C_{13}H_{12}N_4O_6$ requires C, 48.8; H, 3.8; N, 17.5%); $\nu_{max.}$ 3 265 (NH), 1 692 (CO), 1 662 (CO), 1 586, and 1 334 cm^{-1}; δ 2.42 (3 H), 2.48 (3 H), 7.22 (1 H, d), 8.03 (1 H, d, *J* 10.0 Hz), 8.13 (1 H, d, *J* 10.0 Hz), 8.39 (1 H, dd), 9.12 (1 H, d), and 11.42 (1 H, NH); *m/z* 320 (M^+).

Methoxycarbonylhydrazones (**11b**)—(**11g**): *General Procedures.—Method A.* The hydrazone (**2b**) (5 mmol), the activated methylene compound (8 mmol), and sodium carbonate were stirred together in dichloromethane for the time specified. The product was isolated by column chromatography (silica).

Method B. The hydrazone (**2b**) (5 mmol), the activated methylene compound (8 mmol), acetic acid (10 mmol), and piperidine (10 mmol) were heated in tetrahydrofuran (100 cm^3) under reflux for 0.5 h. The reaction mixture was cooled and filtered. The filtrate was evaporated and the residue was dissolved in ethyl acetate (50 cm^3). The solution was washed with water, dried, and evaporated to dryness; the residue was recrystallised.

(a) 3-*Acetylpent*-2-*ene*-1,4-*dione* 1-*methoxycarbonylhydrazone* (**11b**). Pentane-2,4-dione gave, by method A, the *hydrazone* (**11b**) (58%), m.p. 149—150 °C (from dichloromethane–hexane) (Found: C, 50.9; H, 5.8; N, 13.4. $C_9H_{12}N_2O_4$ requires C, 50.9; H, 5.7; N, 13.2%); $\nu_{max.}$ 3 320 (NH), 1 755 (CO), and 1 685 cm^{-1} (CO); $\lambda_{max.}$(EtOH) 254 (ε 23 000) and 303 nm (23 000); δ 2.38 (3 H), 2.41 (3 H), 3.87 (3 H), 7.38 (1 H, d, *J* 10.0 Hz), 8.01 (1 H, d, *J* 10.0 Hz), and 9.74 (1 H, NH); *m/z* 212 (M^+). The same product (50%) was also obtained by method B.

(b) 3-*Benzoyl*-4-*phenylbut*-2-*ene*-1,4-*dione* 1-*methoxycarbonylhydrazone* (**11c**). Dibenzoylmethane gave, by method B, the *hydrazone* (**11c**) (50%), m.p. 125—127 °C (from toluene) (Found: C, 67.9; H, 4.8; N, 8.4. $C_{19}H_{16}N_2O_4$ requires C, 67.9; H, 4.7; N, 8.3%); $\nu_{max.}$ 3 200 (NH), 1 715 (CO), and 1 670 (CO) cm^{-1}; δ 3.78 (3 H), 7.25—7.85 (12 H, m), and 8.75 (1 H, NH); *m/z* (by chemical ionisation) 337 (M^+ + 1).

(c) *Ethyl* 2-*ethoxycarbonyl*-4-*oxobut*-2-*enoate* 4-*methoxycarbonylhydrazone* (**11d**). Diethyl malonate gave, by method B followed by layer chromatography (silica) and elution with ether–hexane (2:1), the *hydrazone* (**11d**) (25%), m.p. 90—93 °C (from ether–hexane) (Found: C, 48.6; H, 5.9; N, 10.4. $C_{11}H_{16}N_2O_6$ requires C, 48.5; H, 5.9; N, 10.3%); $\nu_{max.}$ 3 200 (NH), 1 720 (CO), and 1 710 cm^{-1} (CO); δ 1.28 (3 H, t), 1.29 (3 H, t), 3.83 (3 H), 4.20 (2 H, q), 4.22 (2 H, q), 7.48 (1 H, d, *J* 9.8 Hz), 8.19 (1 H, d, *J* 9.8 Hz), and 10.11 (1 H, NH); *m/z* 272 (M^+).

(d) 2-*Cyano*-4-*oxobut*-2-*enonitrile* 4-*methoxycarbonylhydrazone* (**11e**). Malononitrile gave, by method B, the *hydrazone* (**11e**) (95%), m.p. 181 °C (decomp.) (from ethyl acetate–hexane) (Found: C, 47.0; H, 3.4; N, 31.4. $C_7H_6N_4O_2$ requires C, 47.2; H, 3.4; N, 31.5%); $\nu_{max.}$ 3 200 (NH) and 2.215 cm^{-1} (CN); δ[$(CD_3)_2CO$] 3.81 (3 H), 7.99 (1 H, d, *J* 9.8 Hz), 8.22 (1 H, d, *J* 9.8 Hz), and 11.0 (1 H, NH); *m/z* 178 (M^+).

(e) *Ethyl* 2-*nitro*-4-*oxobut*-2-*enoate* 4-*methoxycarbonylhydrazone* (**11f**). Ethyl nitroacetate gave, by method B, the *hydrazone* (**11g**) (14%), m.p. 124—125 °C (from ether–hexane) (Found: C, 39.0; H, 4.4; N, 17.0. $C_8H_{11}N_3O_6$ requires C, 39.2; H, 4.5; N, 17.1%); $\nu_{max.}$ 3 220 (NH) and 1 715 (CO) cm^{-1}; δ 1.32 (3 H, t), 3.89 (3 H), 4.33 (2 H, q), 7.51 (1 H, d, *J* 9.8 Hz), 7.78 (1 H, d, *J* 9.8 Hz), and 9.05 (1 H, NH); *m/z* 254 (M^+).

(f) 2,2-*Dimethyl*-5-(2-*oxoethylidene*)-1,3-*dioxane*-4,6-*dione* 2-*methoxycarbonylhydrazone* (**11g**). 2,2-Dimethyl-1,3-dioxane-4,6-dione gave, by method B, the *hydrazone* (**11f**) (90%), m.p. 200 °C (from ethanol) (Found: C, 47.0; H, 4.7; N, 11.0. $C_{10}H_{12}N_2O_6$ requires C, 46.9; H, 4.7; N, 10.9%); $\nu_{max.}$ 3 200 (NH) and 1 720 cm^{-1} (CO); δ[$(CD_3)_2CO$] 1.76 (6 H), 3.82 (3 H), 7.87 (1 H, d, *J* 10.0 Hz), 8.86 (1 H, d, *J* 10.0 Hz), and 11.05 (1 H, NH); *m/z* (by chemical ionisation) 257 (M^+ + 1).

3-*Acetyl*-4-(1-*acetyl*-2-*oxopropyl*)-1-(2,4-*dinitrophenylamino*)-2-*methylpyrrole* (**12a**).—The azo-olefin (**1a**) (0.50 g, 1.95 mmol) and pentane-2,4-dione (0.39 g, 3.9 mmol) were dissolved in dichloromethane (50 cm^3) and the solution was kept at 20 °C for 5 days. Layer chromatography (silica) and elution with ether gave the *pyrrole* (**12a**) (0.675 g, 86%), m.p. 190—191 °C (from dichloromethane–hexane) (Found: C, 53.4; H, 4.3; N, 14.0. $C_{18}H_{18}N_4O_7$ requires C, 53.7; H, 4.5; N, 13.9%); $\nu_{max.}$ 3 300br (NH) and 1 650 cm^{-1} (CO); $\lambda_{max.}$(EtOH) 259 (ε 17 500), 294 (14 700), and 310 nm (14 500); δ 2.01 (6 H), 2.30 (3 H), 2.45 (3 H), 6.31 (1 H, d, Ar 6-H), 6.56 (1 H, 5-H), 8.35 (1 H, dd, Ar 5-H), 9.22 (1 H, d, Ar 3-H), and 10.18 (1 H, NH); δ_C[$(CD_3)_2SO$] 11.0 (q, 2-Me), 23.7 (q, 4-Me), 30.2 (q, 3-Me), 107.0 (s, 4-CH), 114.3 (d, Ar 6-C), 117.2 (s, 4-C), 119.7 (s, 3-C), 121.7 (d, Ar 3-C), 122.6 (d, 5-C), 130.8 (s, Ar 2-C), 136.1 (s, Ar 4-C), 138.0 (s, 2-C), 147.1 (s, Ar 1-C), 191.0 (s, 4-CO), and 193.3 (s, 3-CO) p.p.m.

3-*Acetyl*-4-(1-*acetyl*-2-*oxopropyl*)-1-*methoxycarbonylamino*-2-*methylpyrrole* (**12b**).—A solution of dichloroacetaldehyde methoxycarbonylhydrazone (**2b**) (3.0 g, 16.2 mmol) and pentane-2,4-dione (4.87 g, 48.7 mmol) in dichloromethane (100 cm^3) was stirred with anhydrous sodium carbonate (6 g) for 14 days. Column chromatography (silica) and elution with ether gave the *pyrrole* (**12b**) (2.46 g, 52%), m.p. 151—153 °C (from ethyl acetate–hexane) (Found: C, 57.2: H, 6.3; N, 9.7. $C_{14}H_{18}N_2O_5$ requires C, 57.1; H, 6.1; N, 9.5%); $\nu_{max.}$ 3 180 (NH), 1 750 (CO), and 1 627 cm^{-1} (CO); δ[$(CD_3)_2CO$] 1.89 (6 H), 2.19 (3 H), 2.41 (3 H), 3.77 (3 H), 6.67 (1 H), and 9.66br (1 H, NH); δ_C[$(CD_3)_2CO$] 11.2 (q, 2-Me), 23.9 (q, 4-Me), 30.2 (q, 3-Me), 53.4 (q, 1-Me), 107.0 (s, 4-CH), 117.0 (s, 4-C), 119.5 (s, 3-C), 122.1 (d, 5-C), 138.0 (s, 2-C), 155.6 (s, 1-CO), 191.5 (s, 4-CO), and 195.2 (s, 3-CO) p.p.m.

4,5-*Dihydro*-1-(2,4-*dinitrophenylamino*)-4-*ethoxycarbonyl*-3-(1-*ethoxycarbonyl*-2-*oxopropyl*)-5-*hydroxy*-5-*methylpyrrole* (**14**).—A solution of the azo-olefin (**1a**) (0.50 g, 1.95 mmol) and ethyl acetoacetate (0.50 g, 3.93 mmol) in dichloromethane (50 cm^3) was kept at 20 °C for 4 days. Removal of the solvent gave the *dihydropyrrole* (**14**) (0.75 g, 80%), m.p. 160 °C (decomp.) (from ethanol) (Found: C, 50.3; H, 4.9; N, 11.6. $C_{20}H_{24}N_4O_{10}$ requires C, 50.0; H, 5.0; N, 11.7%); $\nu_{max.}$ 3 420 (OH), 3 330 (NH), 1 700 (CO), and 1 650 cm^{-1} (CO); δ[$(CD_3)_2SO$] 1.19 (6 H, 2 × t), 1.35 (3 H), 2.16 (3 H), 3.05 and 3.08 (ss, together 1 H, 4-H), 3.90—4.20 (5 H, m), 5.64 and 5.67 (ss, together 1 H, 3-CH), 6.13 (1 H, 2-H), 7.66 (1 H, d), 8.24 (1 H, dd), 8.88 (1 H, d), and 9.50 (1 H, NH); *m/z* 462 (M^+ − 18).

1-(2,4-*Dinitrophenylamino*)-3-*ethoxycarbonyl*-4-(1-*ethoxycarbonyl*-2-*oxopropyl*)-2-*methylpyrrole* (**12c**).—The dihydropyrrole (**14**) (0.10 g, 0.21 mmol) was heated in ethanol (25 cm^3) under reflux with sulphuric acid (0.2 g) for 1 h. Water was added until the reaction mixture became turbid, and the mixture was then allowed to cool. The precipitate was filtered off and crystallised to give the *pyrrole* (**12c**) (0.067 g, 70%), m.p. 111—114 °C (from aqueous ethanol) (Found: C, 52.2; H, 5.0; N, 12.1. $C_{20}H_{22}N_4O_9$ requires C, 51.9; H, 4.8; N, 12.1%); δ[$(CD_3)_2CO$] 1.22 (3 H, t), 1.31 (3 H, t), 2.24 (3 H), 2.43 (3 H), 4.19 (2 H, q), 4.26 (2 H, q), 5.43 (1 H, 4-CH), 6.46 (1 H, d, Ar 6-H), 6.90 (1 H, 5-H), 8.43 (1 H, dd), 9.07 (1 H, d), and 10.94 (1 H, NH); *m/z* 462 (M^+).

Bis(4,4-*dimethyl*-2,6-*dioxocyclohexyl*)*acetaldehyde* 2,4-*Dinitrophenylhydrazone* (**13**).—A solution of the azo-olefin (**1a**) (0.30 g, 1.17 mmol) and dimedone (0.66 g, 4.7 mmol) in dichloromethane (50 cm^3) was stirred with sodium carbonate (1 g) for 4 days at 20 °C. The solution was washed with water, dried, and the solvent was removed to give the *hydrazone* (**13**) (0.43 g, 76%), m.p. 176 °C (from dichloromethane–hexane) (Found: C, 57.4; H, 5.6; N, 11.5. $C_{24}H_{28}N_4O_8$ requires C, 57.6; H, 5.6; N, 11.2%); $\nu_{max.}$ 3 290 (NH) and 1 600 cm^{-1} (CO); $\lambda_{max.}$(EtOH) 261 (ε 34 000) and 368 nm (20 000); δ 1.15 (12 H), 2.38 (8 H), 5.03 (1 H, d, *J* 2.0 Hz), 7.61 (1 H, d, *J* 2.0 Hz), 7.75 (1 H, d), 8.27 (1 H, dd), and 9.11 (1 H, d).

6,6-*Dimethyl*-3-(4,4-*dimethyl*-2,6-*dioxocyclohexyl*)-1-(2,4-*dinitrophenylamino*)-4-*oxo*-4,5,6,7-*tetrahydroindole* (**12d**).—A solution of the hydrazone (**13**) (0.10 g, 0.2 mmol) containing 2 drops of concentrated HCl was heated under reflux for 20 min. Hot water was added until the reaction mixture became turbid. It was then cooled and the precipitate was filtered off and crystallised to give the *tetrahydroindole* (**12d**) (0.53 g, 55%), m.p. 235 °C (decomp.) (from dichloromethane–hexane) (Found: C, 59.3; H, 5.1; N, 11.7. $C_{24}H_{26}N_4O_7$ requires C, 59.7; H, 5.4; N, 11.7%); $\nu_{max.}$ 3 280 (NH), 1 617 (CO), and 1 595 cm^{-1} (CO); δ 1.09 (12 H), 2.34 (2 H), 2.40—2.60 (6 H, m), 6.52 (1 H, d, Ar 6-H), 6.94 (1 H, 5-H), 8.34 (1 H, dd), 9.18 (1 H, d), and 9.74 (1 H, NH); δ_C[$(CD_3)_2SO$] 28.0 (q), 31.4 (s), 33.8—52.3 (m), 108.1 (s, 2-C of C-4 substituent), 114.7 (d, Ar 6-C), 116.6 (s, 3-C), 121.9 (d, Ar 3-C), 122.6 (d, 5-C), 130.3 (s, Ar 2-C), 130.5 (d, Ar 5-C), 137.8 (s, Ar 4-C), 141.5 (s, 2-C), 147.4 (s, Ar 1-C), 191.1 (s), and 194.5 (s).

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