Cycloaddition Reactions of Nitrosoalkenes and Azoalkenes with Cyclopentadiene and Other Dienes [1]

By **Roy Faragher** and **Thomas L. Gilchrist,*** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

α-Nitrosostyrene, when generated from α-chloroacetophenone oxime in the presence of cyclopentadiene, forms a 1 : 1 adduct. This adduct has been formulated as the oxazine derivative (1a) which is formally derived from its two components by 4 + 2 cycloaddition, the nitrosoalkene acting as the 4-electron component. Several similar reactions have been observed between this and related nitrosoalkenes and dienes. Indene and α-morpholinostyrene add in a similar way to α-nitrosostyrene. 2,2-Dichloronitrosoethylene is exceptional in forming a different type of adduct (9) with cyclopentadiene; the reasons for this are discussed. Azoalkenes $H_2C{=}C(Ph)N{=}NX$ undergo cycloaddition with cyclopentadiene in an analogous manner to that of α-nitrosostyrene, giving pyridazine derivatives (11). Several similar additions of azoalkenes to electron-rich dienes and olefins have been observed, the ease of the reactions reflecting the strength of the frontier orbital interaction between the two components.

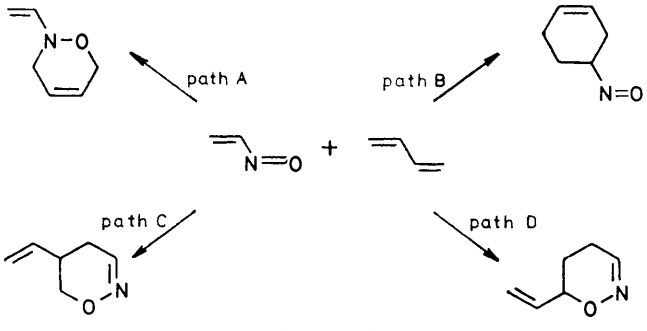
CYCLOADDITION reactions in which a nitroso- or azo-group participates as the 2π-electron component have been known for several years.[2] Recently the range of such reactions has been extended by the observations that nitrosocarbonyl compounds,[3] nitroso-imines,[4] and nitrosyl cyanide [5] readily undergo Diels–Alder addition to dienes. As a result of some earlier work involving the generation of nitrosoalkenes and azoalkenes as reaction intermediates,[6] we considered the possibility of intercepting these species by a cycloaddition process. When we started the investigation, no cycloadditions of nitrosoalkenes had been reported, although an attempt had been made to observe such a reaction between nitrosocyclohexene and maleic anhydride.[7] A few examples of the addition of azoalkenes to electron-deficient dienophiles were known.[8]

Nitrosoalkenes have been isolated in only a few cases,[9] where the presence of bulky substituents at the β-carbon atom lowers their reactivity. Normally they are observed only in solution, their presence sometimes being detectable by a blue colouration (they have a $\lambda_{max.}$ close to 700 nm).[10] The usual method of generating them is the elimination of hydrogen halide from α-halogenoketoximes, and this procedure has been used in the present work. Some α-chloroketoximes have been shown to be quite acidic, with pK_a values in the region of 3—4,[10] and a base such as triethylamine or sodium carbonate is strong enough to generate the nitrosoalkenes. Azoalkenes are generally more stable, and many have been isolated. The absence of substituents at the β-carbon atom lowers their stability; thus, α-(phenylazo)-styrene dimerises rapidly at low temperatures.[11] Such unstable azoalkenes can be generated in a manner analogous to that for nitrosoalkenes, by the base-induced elimination of hydrogen halide from hydrazone derivatives of α-halogenoketones, and we have made use of this method.

RESULTS AND DISCUSSION

Cycloadditions of Nitrosoalkenes.—The various types of cycloaddition reaction between a nitrosoalkene and a diene are illustrated in Scheme 1 for nitrosoethylene and butadiene. Addition of the diene to the nitroso-group (path A) is the mode of reaction to be expected by analogy with the behaviour of other nitroso-compounds; addition to the C=C bond (path B) corresponds to the common mode of addition of nitroalkenes and of αβ-unsaturated carbonyl compounds. Addition of nitrosoethylene as a 4π component (paths C and D) has an analogy in the cycloadditions of *N*-alkyl-*N*-vinylnitrosonium ions to alkenes, recently studied by Eschenmoser and his co-workers.[12]

As a guide to which of these reaction paths we might expect to occur, we compared the frontier orbital



SCHEME 1

energies and orbital coefficients of nitrosoethylene and butadiene. The values for nitrosoethylene were obtained using a CNDO/2 [13] programme and those for butadiene were from the literature. The relative orbital energies indicate that the major interaction is likely to be that between the highest-occupied molecular orbital of butadiene and the lowest-unoccupied molecular orbital of nitrosoethylene; *i.e.* butadiene acts as the donor and nitrosoethylene as the acceptor. Of the various possible modes of addition outlined in Scheme 1, the most favourable appear to be those involving an interaction between C-2 of nitrosoethylene and C-1 of butadiene, *i.e.* paths B and D. Path B, involving addition of the diene to the C=C bond, is slightly the more favourable of the two on the basis of the coefficients shown, but it hardly seems reasonable to try to distinguish between the two possible pathways in terms of small differences in coefficients. Such a distinction has

been made [14] in an analysis of the analogous cycloaddition of acrylaldehyde to butadiene, in which the calculated energies and coefficients for the frontier orbitals of acrylaldehyde are very similar to those of nitrosoethylene. The authors conclude that their calculations indicate a clear preference for addition to the double C=C bond of acrylaldehyde, which is the mode of addition actually observed.

We chose to investigate the addition of nitrosoethylene and other simple nitrosoalkenes to dienes. Solutions containing the appropriate chloro-oximes and an excess of the diene in dichloromethane were stirred with anhydrous sodium carbonate at 20 °C for 24 h. The results

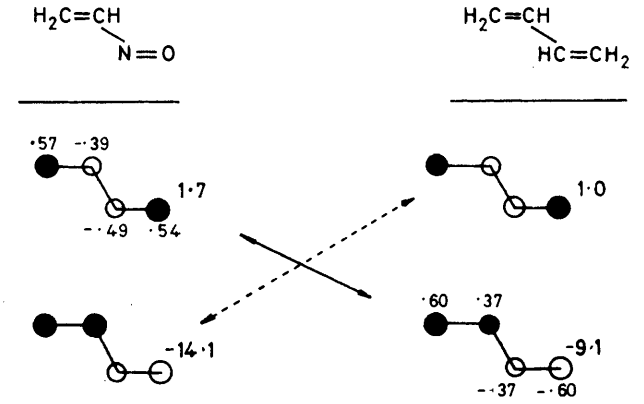


FIGURE Frontier orbital energies (eV) and coefficients for nitrosoethylene and butadiene

of these reactions, and the products isolated, are listed in Table 1. Nitrosoethylene formed an adduct with

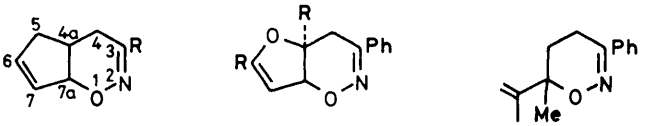
TABLE 1

Reactions of nitrosoalkenes $R^1R^2C{=}CR^3NO$ [a] with olefins and dienes

R^1	R^2	R^3	Olefin or diene	Product	% Yield
H	H	Ph	Cyclopentadiene	(1a)	90
H	H	C_6H_4Br-4	Cyclopentadiene	(1b)	79
H	H	2-furyl	Cyclopentadiene	(1c)	62
H	H	H	Cyclopentadiene	(1d)	19
Cl	Cl	H	Cyclopentadiene	(9)	50
H	$-[CH_2]_4-$		Cyclopentadiene	*b*	
H	H	P	Furan	(2a)	45
Cl	Cl	H	Furan	*b*	
H	H	Ph	2,5-Dimethylfuran	(2b)	44
H	H	Ph	2,3-Dimethylbutadiene	(3)	41
Cl	Cl	H	1,3-Cyclohexadiene	*c*	
Cl	Cl	H	6,6-Dimethylfulvene	*c*	
H	H	Ph	Indene	(6)	26
Cl	Cl	H	Indene	*b*	
H	H	Ph	α-Morphlinostyrene	(7)	26

[a] Generated *in situ* from the corresponding α-chloro-oximes and sodium carbonate. [b] No adduct was detected. [c] Addition took place but the product was not characterised.

cyclopentadiene which was volatile and rather unstable, so most additions were carried out using α-nitrosostyrene, which gave stable crystalline adducts. The ^1H n.m.r. spectra showed that all the adducts had closely related structures; these were formulated as the oxazine derivatives (1a), (2), and (3). The spectrum of the adduct (2b) formed from 2,5-dimethylfuran shows two doublets (J 14 Hz) at δ 2.57 and 3.01 for the hydrogen atoms at C-4; the methyl groups appear at δ 1.49 and 1.72. The furan adduct (2a) shows similar signals for



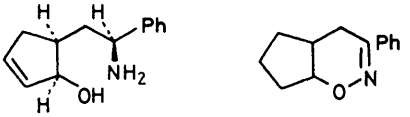
(1) a; R = Ph
b; R = C_6H_4Br-4
c; R = 2-furyl
d; R = H

(2) a; R = H
b; R = Me

(3)

the geminal hydrogen atoms at C-4 but these are now further split by coupling to the hydrogen at C-4a. Signals at δ 6.53 and 5.36 are assigned to the hydrogen atoms at C-6 and C-7, respectively; those at C-4a and C-7a appear as a multiplet at δ 5.14—5.25. The spectrum of the cyclopentadiene adduct (1a) is clearly incompatible with a structure in which addition has taken place across the 1- and 4-positions of the diene; the signals of the hydrogen atoms at C-6 and C-7 appear as doublets (J 6 Hz) between δ 5.74 and 6.10, each doublet showing further splitting. The adduct (3) formed from 2,3-dimethylbutadiene shows signals for the methyl groups at δ 1.42 and 1.77, and for the terminal hydrogen atoms of the isopropenyl group as singlets at δ 4.90 and 5.03.

Support for the proposed structure of the furan adduct (2a) comes from its acid-catalysed rearrangement to α-(2-furyl)acetophenone oxime.[15] Evidence for the structure (1a) assigned to the adduct of cyclopentadiene with α-nitrosostyrene was obtained by its reductive cleavage with lithium aluminium hydride, which gave, in good yield, a mixture of diastereoisomeric aminocyclopentenols. Repeated crystallisation of the mixture gave a sharp-melting crystalline solid for which the analytical and spectral data are in accord with structure (4). Catalytic hydrogenation of the oxazine (1a) at

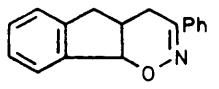


(4) (5)

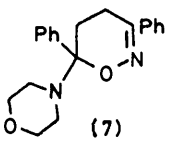
atmospheric pressure resulted in the uptake of 1 mol of hydrogen at the C=C bond, giving the oxazine derivative (5) as a crystalline solid.

In these cycloadditions the nitrosoalkenes are formally acting as 4π-electron components and the dienes as 2π-electron components. There are several ways in which such adducts could be formed. A concerted Diels–Alder cycloaddition of the nitrosoalkenes, acting as electron-deficient 4π-electron systems, and the dienes, acting as electron-rich 2π-electron systems, could give these products. A stepwise addition *via* a zwitterionic intermediate is also possible. The observations that both indene and α-morpholinostyrene also give oxazines (6) and (7) with α-nitrosostyrene are compatible with either

of these mechanisms. A third possibility is that the initial addition to dienes involves the nitrosoalkenes acting as 2π-electron components *via* the C=C bond, but that these adducts undergo a [3,3] sigmatropic



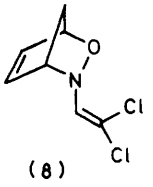
(6)



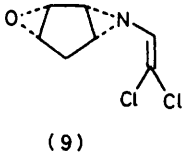
(7)

rearrangement to give the observed products. There are good analogies for such a facile rearrangement,[16] but we have no positive evidence to support such a proposal at present.

Since the mode of addition of these nitrosoalkenes to dienes was different from that of all other types of nitroso-compound, we thought that we might be able to observe the more usual mode of addition by changing the substituents of the nitrosoalkene. 2,2-Dichloronitrosoethylene was selected for study since the dichlorovinylidene group sometimes mimics an oxo-group in organic reactions; thus this nitrosoalkene should behave more like a nitrosocarbonyl compound. Indeed, the adduct formed from cyclopentadiene was clearly different from those obtained earlier with other nitrosoalkenes: the n.m.r. spectrum indicated the absence of double bonds, and chemical tests indicated the presence of an epoxide function. The adduct has since independently been shown to have the structure (9) on the basis of an



(8)

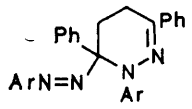


(9)

X-ray study; it is derived from an unstable primary adduct (8).[17] We found that 2,2-dichloronitrosoethylene also reacts with several other dienes but the adducts proved to be very unstable and we have so far been unable to characterise them. No adduct was obtained with indene.

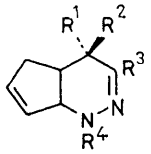
The detection of the adduct (8) in the reaction of this nitrosoalkene with cyclopentadiene [17] shows that a different mode of addition to dienes can be observed. Clearly, the nitrosoalkene substituents play a crucial role. The possible variations are limited by the instability and low reactivity towards dienes of some nitrosoalkenes; for example, we could not obtain an adduct from cyclopentadiene and nitrosocyclohexane. Our current work is aimed at delineating the role of substituents in these additions and the details of the reaction mechanisms.

Cycloadditions of Azoalkenes.—We set out to investigate whether azoalkenes which were structurally similar to α-nitrosostyrene would react with dienes in a similar way. The azoalkenes $H_2C{=}C(Ph)N{=}NX$ (X = 2,4-dinitrophenyl, tosyl, and ethoxycarbonyl) were generated *in situ* from the appropriate hydrazone derivatives of α-bromo- or α-chloro-acetophenone and sodium carbonate at 20 °C. In the absence of a suitable trapping agent, the 2,4-dinitrophenyl derivative gave a cyclic dimer (10) in high yield; in this it resembles α-(phenylazo)-



(10) Ar = $C_6H_3(NO_2)_2$-2,4

styrene.[11] When the azoalkene was generated in the presence of cyclopentadiene, a crystalline adduct was obtained in excellent yield. This was assigned the structure (11a) mainly on the basis of its ^1H n.m.r.



(11) a; $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = C_6H_3(NO_2)_2$-2,4
b; $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = Ts$
c; $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = CO_2Et$
d; $R^1 = R^2 = H$, $R^3 = Me$, $R^4 = C_6H_3(NO_2)_2$-2,4
e; $R^1 = H$, $R^2 = CO_2Et$, $R^3 = Me$, $R^4 = C_6H_3(NO_2)_2$-2,4
f; $R^1 = H$, $R^2 = CO_2Et$, $R^3 = Me$, $R^4 = C_6H_4NO_2$-4
g; $R^1 = CO_2Et$, $R^2 = H$, $R^3 = Me$, $R^4 = Ph$
h; $R^1 = H$, $R^2 = CO_2Et$, $R^3 = Me$, $R^4 = Ph$
j; $R^1 = R^2 = H$, $R^3 = Me$, $R^4 = Ph$

spectrum, which was very similar to that of the corresponding adduct of α-nitrosostyrene. Other addition reactions of this and related azoalkenes to dienes followed a very similar course: the results of these experiments are summarised in Table 2. Most of the additions to electron-rich dienes gave adducts in good yields at room temperature. This was particularly so with azoalkenes bearing an electron-withdrawing group on the azo-function.

The addition of 2-(phenylazo)propene and of ethyl 3-(phenylazo)but-2-enoate to cyclopentadiene was less efficient. The latter compound, which is an isolable solid, did not react with furan, and reacted only slowly with cyclopentadiene at room temperature; the reaction was carried out more satisfactorily by heating the azoalkene with cyclopentadiene in tetrahydrofuran under reflux for 18 h. The adduct obtained at room temperature was a mixture of two isomers, as indicated by the n.m.r. spectrum which showed two very similar sets of signals, but this mixture was converted into a single isomer by heating it at 120 °C for a short time, or by dissolving it in tetrahydrofuran containing a few drops of hydrochloric acid. The two isomers originally present are presumed to be the *exo* and *endo* esters (11g) and (11h), which can be interconverted through an enamino-tautomer (Scheme 2). For the more stable isomer, the coupling constant of H-4 and H-4a was 7.4 Hz. This is better accommodated by structure (11h), in which the ester group can occupy an equatorial position *cis* to the adjacent cyclopentene ring. The

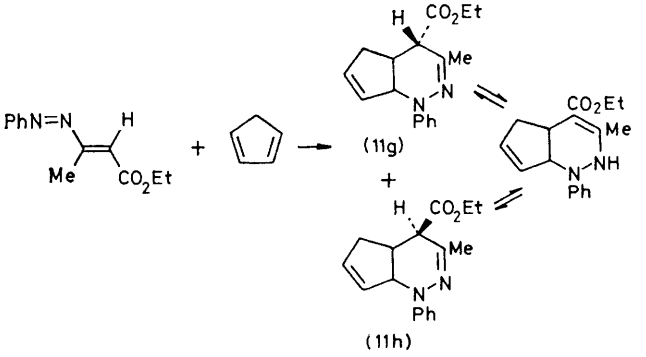
TABLE 2

Reactions of azoalkenes $R^1R^2C{=}C(R^3)N{=}NR^4$ [a] with olefins and dienes

R^1	R^2	R^3	R^4	Olefin or diene	Product	% Yield
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	Cyclopentadiene	(11a)	96
H	H	Ph	Ts	Cyclopentadiene	(11b)	72
H	H	Ph	CO_2Et	Cyclopentadiene	(11c)	96
H	H	Me	$C_6H_3(NO_2)_2$-2,4	Cyclopentadiene	(11d)	78
H	CO_2Et	Me	$C_6H_3(NO_2)_2$-2,4	Cyclopentadiene	(11e)	83
H	CO_2Et	Me	$C_6H_4NO_2$-4 [b]	Cyclopentadiene	(11f)	88
H	CO_2Et	Me	Ph [b]	Cyclopentadiene	(11h)	61
H	H	Me	Ph	Cyclopentadiene	(11j)	14
H	$-[CH_2]_4-$		Ph [b]	Cyclopentadiene	*c*	
Ph	Ph	H	Ts [b]	Cyclopentadiene	*c*	
Cl	Cl	H	$C_6H_3(NO_2)_2$-2,4 [b]	Cyclopentadiene	*c*	
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	2,3-Dimethylbutadiene	(12)	67
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	Furan	(13a)	89
H	H	Me	$C_6H_3(NO_2)_2$-2,4	Furan	(13c)	22
H	CO_2Et	Me	Ph [b]	Furan	*c*	
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	2,5-Dimethylfuran	(13b)	87
H	H	Me	$C_6H_3(NO_2)_2$-2,4	6,6-Dimethylfulvene	(14)	68
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	1-Methoxy-3-trimethylsilyloxy-1,3-butadiene	(15)	32
H	H	Ph	$C_6H_3(NO_2)_2$-2,4	Cyclopentene	(16)	20
					(10)	75
H	H	Me	$C_6H_3(NO_2)_2$-2,4-	α-Morpholinostyrene	(21)	55

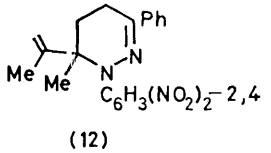
[a] Generated *in situ*, expected where indicated otherwise. [b] Isolated azoalkene was used. [c] No adduct was detected.

coupling constant of 9.8 Hz for the bridgehead hydrogens H-4a and H-7a also indicates that the ring junctions are *cis*.

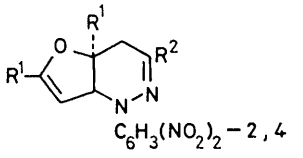


SCHEME 2

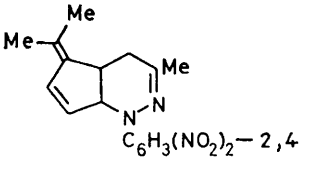
The formation of two stereoisomers at room temperature may indicate that this reaction is not concerted, in



(12)



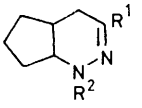
(13) a; R^1 = H, R^2 = Ph
b; R^1 = Me, R^2 = Ph
c; R^1 = H, R^2 = Me



(14)

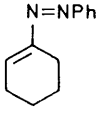
contrast to others of a similar type which have been reported recently.[18] The reasons for this, and the influence of substituents on the mechanisms of these reactions, are currently being investigated.

The adduct (11h) was hydrolysed and decarboxylated to give the tetrahydropyridazine (11j) which had been prepared independently from 2-(phenylazo)propene and cyclopentadiene. This adduct took up one mol of hydrogen on catalytic hydrogenation to give (17) as a crystalline solid. A similar pair of isomers was also formed in the reaction of ethyl 3-(2,4-dinitrophenylazo)-but-2-enoate with cyclopentadiene at room temperature.

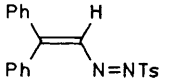


(16); R^1 = Ph, R^2 = $C_6H_3(NO_2)_2$-2,4

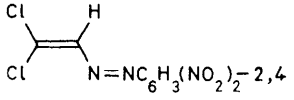
(17); R^1 = Me, R^2 = Ph



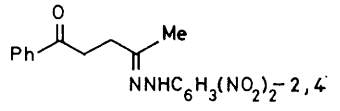
(18)



(19)



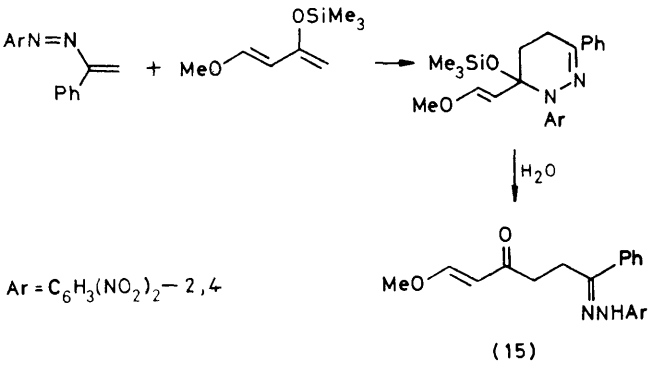
(20)



(21)

The azoalkenes (18), (19), and (20) failed to give adducts with cyclopentadiene. α-(2,4-Dinitrophenylazo)styrene gave an open-chain adduct (15) with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene; this may be formed by hydrolysis of a primary cycloadduct (Scheme 3). This azoalkene was also found to react with cyclopentene, albeit rather inefficiently; the cycloadduct (16) was isolated (20%) together with the dimer

(10) (75%). With the enamine α-morpholinostyrene, 2-(2,4-dinitrophenylazo)propene gave an open-chain adduct (21) after chromatography of the reaction product mixture.



(15)

SCHEME 3

The pattern which emerges from these experiments is that electron-deficient azoalkenes will add to electron-rich dienes and olefins as 4π-electron components, the efficiency of the reaction reflecting the donor–acceptor relationship of the two components. Since our preliminary publication, several other examples, of this type of reaction of azoalkenes have been reported.[18,19] Sommer [18] has recognised two distinct classes of cycloaddition of azoalkenes: reactions in which the azoalkenes act as electron donors, and electron-deficient olefins act as electron acceptors, and those (like the reactions described above) in which the donor–acceptor relationship is reversed. Azoalkenes are potentially very versatile components in cycloaddition reactions, and like the nitrosoalkenes, represent a useful starting point for exploring the preparation and properties of new heterocyclic systems.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained, except where indicated otherwise, at 220 MHz in $CDCl_3$. Mass spectra were recorded at 70 eV using a direct-insertion probe. Preparative layer chromatography was carried out with silica gel GF_{254} (Merck) as the stationary phase. Dichloromethane was dried by distillation from calcium hydride and was stored over molecular sieves (4 Å); tetrahydrofuran was distilled from lithium aluminium hydride and was stored over molecular sieves (4 Å).

Oximes.—Oximes of the following α-halocarbonyl compounds were prepared by literature procedures: α-chloroacetophenone,[20] α,4′-dibromoacetophenone,[20] chloral,[21] chloroacetaldehyde,[21] and 2-chlorocyclohexanone.[22]

2-Bromoacetylfuran oxime. 2-Bromoacetylfuran [23] (3.9 g, 0.02 mol) and hydroxylammonium sulphate (10.3 g, 0.063 mol) gave, in aqueous methanol at 20 °C, the *oxime* (2.1 g, 51%), m.p. 235—237 °C (from chloroform) (Found: C, 35.6; H, 2.9; N, 6.6. $C_6H_6BrNO_2$ requires C, 35.3; H, 3.0; N, 6.9%); δ 4.34 (2 H), 6.50 (1 H, m), 6.77 (1 H, d, *J* 3 Hz), and 7.50 (1 H).

Azoalkenes.—The following azoalkenes were prepared and isolated using literature procedures: 2-(phenylazo)-propene,[24] 1,1-diphenyl-2-(tosylazo)ethene (19),[25] 1-(phenylazo)cyclohexene (18),[26] ethyl 3-(phenylazo)but-2-enoate,[27] and ethyl 3-(4-nitrophenylazo)but-2-enoate.[28]

Other Compounds.—The following were prepared by the literature procedures: the 2,4-dinitrophenylhydrazones of α-bromoacetophenone,[29] chloroacetone,[30] and chloral,[31] and the tosylhydrazone of α-chloroacetophenone.[32]

Ethyl α-chloroacetoacetate 2,4-dinitrophenylhydrazone. This was prepared in the standard way, m.p. 101—102 °C (from ethanol) (Found: C, 42.1; H, 3.9; N, 16.5. $C_{12}H_{13}ClN_4O_6$ requires C, 41.8; H, 3.8; N, 16.3%).

α-Chloroacetophenone ethoxycarbonylhydrazone. This was prepared in the standard way (73%), as a mixture of *syn* and *anti* isomers, as shown by the n.m.r. spectrum. This mixture was used to generate the azoalkene. Several recrystallisations of the mixture gave a specimen with m.p. 115—122 °C (from ethanol) (Found: C, 54.8; H, 5.5; N, 11.5. $C_{11}H_{13}ClN_2O_2$ requires C, 54.9; H, 5.5; N, 11.6%); δ (60 MHz) 1.20 (3 H, t, *J* 6.7 Hz), 4.07 (2 H, q, *J* 6.7 Hz), 4.33 (2 H), 7.04—7.47 (4 H, m), and 7.55—7.80 (1 H, m).

1,1-Dichloro-2-(2,4-dinitrophenylazo)ethene (20). Chloral 2,4-dinitrophenylhydrazone (0.20 g, 0.6 mmol) in tetrahydrofuran (50 cm^3) was stirred at 20 °C with anhydrous sodium carbonate (0.65 g). After 24 h the mixture was filtered and the filtrate was evaporated to dryness. Crystallisation of the residue gave the *azoalkene* (20) (0.11 g, 61%), m.p. 108—110 °C (from ethanol) (Found: C, 33.1; H, 1.5; N, 19.5. $C_8H_4Cl_2N_4O_4$ requires C, 33.0; H, 1.4; N, 19.3%); $\lambda_{max.}$ (EtOH) 332 nm (ε 15 000).

1-(2,4-Dinitrophenyl)-6-(2,4-dinitrophenylazo)-3,6-diphenyl-1,4,5,6-tetrahydropyridazine (10). Anhydrous sodium carbonate (0.3 g) was added to a stirred solution of α-bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) in tetrahydrofuran (70 cm^3). After 20 h the solvent was removed and the residue was shaken with ether and water. The ethereal solution was evaporated to dryness to give the *pyridazine* (10) (0.15 g, 95%), m.p. 180 °C (decomp.) (from dichloromethane–hexane) (Found: C, 56.1; H, 3.3; N, 19.0. $C_{28}H_{20}N_8O_8$ requires C, 56.4; H, 3.4; N, 18.8%); δ 2.25—2.45 (1 H, m), 2.50—2.70 (1 H, m), 2.75—2.90 (1 H, m), 3.05—3.15 (1 H, m), 6.47 (1 H, d, *J* 9 Hz), 7.32—7.50 (6 H, m), 7.54—7.65 (3 H, m), 7.73 (2 H, d, *J* 7 Hz), 7.85 (1 H, dd, *J* 10 and 3 Hz), 8.55 (1 H, d, *J* 3 Hz), 8.58 (1 H, dd, *J* 10 and 3 Hz), and 8.85 (1 H, d, *J* 3 Hz); *m/e* 401 $[M - C_6H_3(NO_2)_2N_2]^+$.

Reactions of Nitrosoalkenes with Olefins and Dienes. General Procedure.—The appropriate α-halogeno-oxime (0.2 g) was dissolved in dichloromethane and an excess (as indicated below) of the trapping agent was added. Anhydrous sodium carbonate (0.6 g) was then added and the suspension was stirred at 20 °C for 20—24 h. The mixture was filtered through Celite, the solvent was removed, and the residue was subjected to thin layer chromatography. Chloroform–ethyl acetate (19 : 1) was used as the eluant.

The following adducts were prepared by this general method.

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and cyclopentadiene (1 cm^3, 12.2 mmol) gave *3-phenyl-4,4a,5,7a-tetrahydrocyclopent*[e]*-1,2-oxazine* (1a) (0.214 g, 90%), m.p. 79—80 °C (from pentane) (Found: C, 78.6; H, 6.5; N, 7.3. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%); δ (100 MHz) 2.08—2.98 (5 H, m), 4.87—5.04 (1 H, d, $J_{4a,7a}$ 7 Hz, H-7a; d shows further splitting), 5.80 (1 H, dd showing further splitting, $J_{6,7}$ 6 Hz, $J_{5,6}$ 2 Hz, H-6), 6.03 (1 H, d showing further splitting, $J_{6,7}$ 6 Hz, H-7),

7.29—7.44 (3 H, m), and 7.62—7.77 (2 H, m); *m/e* 199 (M^+), 181, and 103 (base).

α,4′-Dibromoacetophenone oxime (0.2 g, 0.68 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 3-(4-*bromophenyl*)-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (1b) (0.151 g, 79%), m.p. 105—106 °C (from ethanol) (Found: C, 55.9; H, 4.2; N, 4.8. $C_{13}H_{12}BrNO$ requires C, 56.1; H, 4.4; N, 5.0%); δ 2.20 (1 H, d, *J* 16 Hz, *endo*-H-6), 2.42 (1 H, dd, *J* 15 and 7 Hz), 2.64—3.00 (3 H, m), 4.98 (1 H, d, $J_{4a,7a}$ 8 Hz, H-7a), 5.80—5.87 (1 H, m, H-6), 6.02—6.08 (1 H, m, H-7), and 7.50—7.63 (4 H, m); *m/e* 279 (M^+) and 78 (base).

2-Bromoacetylfuran oxime (0.2 g, 0.98 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 3-(2-*furyl*)-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (1c) (0.115 g, 62%), m.p. 87 °C (decomp.) (from dichloromethane–hexane) (Found: C, 69.7; H, 5.9; N, 7.2. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.9; N, 7.4%); δ 2.23 (1 H, d, *J* 17 Hz), 2.34 (1 H, dd, *J* 13.4 and 7 Hz), 2.60—3.00 (3 H, m), 5.00 (1 H, d, $J_{4a,7a}$ 7.8 Hz, H-7a), 5.83 (1 H, m, H-6), 6.04 (1 H, m, H-7), 6.47 (1 H, m), 6.83 (1 H, d, *J* 3.4 Hz), and 7.52 (1 H); *m/e* 189 (M^+, base).

α-Chloroacetaldehyde oxime (0.2 g, 2.1 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 4,4a,5,7a-tetrahydrocyclopent[*e*]-1,2-oxazine (1d) (0.05 g, 19%) as a colourless oil which gradually turned brown on standing; it was not completely characterised, δ (60 MHz) 2.00—5.00 (5 H, m), 4.70—4.96 (1 H, m, H-7a), 5.80—5.97 (1 H, m, H-6), 6.10—6.27 (1 H, m, H-7), and 7.83—7.97 (1 H, m, H-3).

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and furan (5 cm³) gave 3-*phenyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (2a) (0.106 g, 45%), m.p. 71—72 °C (from pentane) (Found: C, 71.7; H, 5.6; N, 7.1. $C_{12}H_{11}NO_2$ requires C, 71.6; H, 5.5; N, 7.0%); $\nu_{max.}$ 1 618s cm⁻¹; δ 2.78 (1 H, dd, J_{gem} 14, $J_{4,4a}$ 4 Hz, *exo*-H-4), 3.08 (1 H, dd, *J* 14 and 4 Hz, *endo*-H-4), 5.14—5.25 (2 H, m, H-4a and H-7), 5.36 (1 H, dd, $J_{7,7a}$ 3 Hz, $J_{4a,7a}$ 9 Hz, H-7a), 6.53 (1 H, d, $J_{6,7}$ 3 Hz, H-6), 7.30—7.50 (3 H, m), and 7.65—7.77 (2 H, m); *m/e* 201 (M^+), 183, and 103 (base).

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and 2,5-dimethylfuran (1.26 cm³, 11.9 mmol) gave 4a,6-*dimethyl*-3-*phenyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (2b) (0.12 g, 44%), m.p. 62—64 °C (from pentane) (Found: C, 73.1; H, 6.5; N, 6.5. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%); $\nu_{max.}$ 1 660s cm⁻¹; δ (100 MHz) 1.49 (3 H, Me-4a), 1.72 (3 H, Me-6), 2.57 (1 H, d, J_{gem} 14 Hz, *exo*-H-4), 3.01 (1 H, d, *J* 14 Hz, *endo*-H-4), 4.67—4.77 (1 H, m, H-7a), 4.83—4.92 (1 H, m, H-7), 7.33—7.46 (3 H, m), and 7.59—7.77 (2 H, m); *m/e* 229 (M^+), 212, and 96 (base).

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and 2,3-dimethylbutadiene (0.7 cm³, 6.2 mmol) gave 6-*methyl*-3-*phenyl*-6-α-*methylvinyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3) (0.015 g, 41%), m.p. 48—51 °C (from pentane) (Found: C, 78.0; H, 7.9; N, 6.5. $C_{14}H_{17}NO$ requires C, 78.1; H, 8.0; N, 6.5%); δ 1.42 (3 H), 1.77 (3 H), 1.80—1.92 (1 H, m), 2.19—2.32 (1 H, m), 2.40—2.52 (2 H, m), 4.90 (1 H), 5.03 (1 H), 7.30—7.36 (3 H, m), and 7.63—7.70 (2 H, m); *m/e* 215 (M^+) and 185 (base).

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and indene (0.7 cm³, 6.0 mmol) gave 3-*phenyl*-4,4a,5,9b-*tetrahydroindeno*[2,3-e]-1,2-*oxazine* (6) (0.077 g, 26%), m.p. 140—143 °C (from ethanol) (Found: C, 82.1; H, 6.1; N, 5.8. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.1; H, 5.6%); δ 2.44 (1 H, q, *J* 8.8 Hz), 2.85—3.10 (3 H, m), 3.30 (1 H, dd, *J* 15.6 and 7.2 Hz), 5.22 (1 H, d, *J* 6 Hz, H-9b), 7.23—7.35 (3 H, m), 7.37—7.49 (3 H, m), 7.53—7.66 (1 H, m), and 7.70—7.80 (2 H, m); *m/e* 249 (M^+), 232, and 231.

α-Chloroacetophenone oxime (0.2 g, 1.18 mmol) and α-morpholinostyrene (0.22 g, 1.16 mmol) gave, by direct recrystallisation of the crude reaction product, 6-*morpholino*-3,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (7) (0.098 g, 26%), m.p. 187—188 °C (from benzene–hexane) (Found: C, 74.7; H, 6.9; N, 8.9. $C_{20}H_{22}N_2O_2$ requires C, 74.5; H, 6.9; N, 8.7%); δ (100 MHz) 1.83—3.08 (8 H, m), 3.59 (4 H, t, *J* 4 Hz), 7.22—7.39 (8 H, m), and 7.55—7.67 (2 H, m); *m/e* 322 (M^+), 305, and 220 (base).

Chloral oxime (0.2 g, 1.23 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 7-(2,2-dichlorovinyl)-7-aza-3-oxatricyclo[4.1.0.0^{2,4}]heptane (9) as a colourless oil (0.118 g, 50%) which crystallised when set aside for several weeks at 0 °C; m.p. 55—56 °C (from pentane) (lit.,[17] 52—53 °C) (Found: C, 43.8; H, 3.5; N, 7.0. Calc. for $C_7H_7Cl_2NO$: C, 43.8; H, 3.7; N, 7.3%); *m/e* 191 (M^+), 163, 138, 122, 81, and 66 (base).

Reduction of the Adduct (1a).—(*a*) *Reduction with lithium aluminium hydride.* The oxazine (1a) (1.0 g, 5.0 mmol) was reduced by the addition of lithium aluminium hydride (0.5 g, 13.2 mmol) in ether at 20 °C. This gave an oily solid (0.84 g, 82%). Three recrystallisations from ether and two from dichloromethane–hexane gave 5-(2-*amino*-2-*phenylethyl*)*cyclopent*-2-*enol* (4), m.p. 116.5—117.5 °C (Found: C, 76.9; H, 8.3; N, 6.8. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%); $\nu_{max.}$ 3 370, 3 100, and 1 620 cm⁻¹; δ 1.90—2.50 (8 H, m, reduces to 5 H, m, after shaking with D_2O), 4.12 (1 H, t, *J* 4.9 Hz), 4.56 (1 H, m), 5.90 (1 H, m), 5.95 (1 H, m), 7.20—7.30 (1 H, m), and 7.36 (4 H, m); *m/e* 203 (M^+), 185, and 106 (base).

(*b*) *Catalytic hydrogenation.* The oxazine (1a) (0.3 g, 0.15 mmol) in ethanol (30 cm³) was reduced by hydrogenation over 5% Pd–C (0.03 g) to give, after t.l.c., 3-*phenyl*-4,4a,5,6,7,7a-*hexahydrocyclopent*[e]-1,2-*oxazine* (5) (0.20 g, 66%), m.p. 46—47 °C (from pentane) (Found: N, 6.9. $C_{13}H_{15}NO$ requires N, 7.0%); δ 1.50—1.70 (2 H, m), 1.80—2.10 (4 H, m), 2.30—2.45 (2 H, m), 2.85 (1 H, dd, *J* 17.1 and 9.8 Hz), 4.07 (1 H, m), 7.35—7.50 (3 H, m), and 7.70—7.80 (2 H, m); *m/e* 201 (M^+), 172, 144, and 130.

Reactions of Azoalkenes with Olefins and Dienes. General Procedure.—The appropriate hydrazone derivative of the α-halogenocarbonyl compound (0.2 g) and an excess of the trapping agent in tetrahydrofuran (50 cm³) were stirred with anhydrous sodium carbonate (0.3 g, 2.8 mmol) at 20 °C for 20—24 h. The solution was then filtered through Celite, the solvent was removed, and the residue was subjected to t.l.c., chloroform being used as the eluant.

This general procedure was used to prepare the adducts described below, unless, as indicated for particular reactions, the azoalkene was a stable isolable compound, in which cases the azoalkene and trapping agent were allowed to react directly.

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 1-(2,4-*dinitrophenyl*-3-*phenyl*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11a) (0.184 g, 96%), m.p. 172—173 °C (from ethyl acetate) (Found: C, 62.9; H, 4.4; N, 15.3. $C_{19}H_{16}N_4O_4$ requires C, 62.6; H, 4.4; N, 15.4%); $\nu_{max.}$ 1 603 cm⁻¹; δ 2.12—3.16 (5 H, m), 5.05 (1 H, d, further split, $J_{4a,7a}$ 8 Hz, H-7a), 5.86 (1 H, m, H-6), 6.06 (1 H, m, H-7), 7.21 (1 H, d, *J* 10 Hz), 7.30—7.43 (3 H, m), 7.50—7.68 (2 H, m), 8.28 (1 H, dd, *J* 10 and 3 Hz), and 8.52 (1 H, d, *J* 3 Hz); *m/e* 364 (M^+), 347, and 103 (base).

α-Chloroacetophenone tosylhydrazone (0.2 g, 0.62 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 3-*phenyl*-1-(4-*tolylsulphonyl*)-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]-*pyridazine* (11b) (0.158 g, 72%), m.p. 167—169 °C (from ethanol) (Found: C, 68.2; H, 5.6; N, 7.8. $C_{20}H_{20}N_2O_2S$ requires C, 68.2; H, 5.7; N, 8.0%); δ 2.04—2.20 (2 H, m), 2.40 (1 H, m), 2.40 (3 H), 2.65 (2 H, dd, *J* 15 and 5 Hz), 4.74 (1 H, br, d, $J_{4a,7a}$ 6 Hz, H-7a), 5.88 (2 H, br, H-6 and H-7), 7.30—7.38 (5 H, m), 7.62—7.70 (2 H, m), and 7.95 (2 H, d, *J* 8.5 Hz); *m/e* 352 (M^+) and 103 (base).

α-Chloroacetophenone ethoxycarbonylhydrazone (0.2 g, 0.83 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 1-*ethoxycarbonyl*-3-*phenyl*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11c) (0.215 g, 96%) as a colourless oil (Found: N, 10.5. $C_{16}H_{18}N_2O_2$ requires N, 10.4%); $\nu_{max.}$ 1 690 cm⁻¹; δ 1.38 (3 H, t, *J* 7.3 Hz), 2.14—2.36 (2 H, m), 2.60—2.80 (3 H, m), 4.37 (2 H, dq, *J* 2.4 and 7.3 Hz), 5.10 (1 H, m, H-7a), 5.88 (1 H, m, H-6), 5.94 (1 H, m, H-7), 7.34—7.44 (3 H, m), and 7.73—7.80 (2 H, m); *m/e* 270 (M^+).

α-Chloroacetone 2,4-dinitrophenylhydrazone (0.2 g, 0.73 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 1-(2,4-*dinitrophenyl*)-3-*methyl*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*-[c]*pyridazine* (11d) (0.174 g, 78%), m.p. 168—169 °C (from ethanol) (Found: C, 55.7; H, 4.4; N, 18.8. $C_{14}H_{14}N_4O_4$ requires C, 55.6; H, 4.7; N, 18.5%); $\nu_{max.}$ 1 613 cm⁻¹; δ 2.00 (3 H), 2.06—2.40 (3 H, m), 2.60—3.12 (2 H, m), 4.97 (1 H, d, br, $J_{4a,7a}$ 8 Hz, H-7a), 5.78 (1 H, m, H-6), 6.05 (1 H, m, H-7), 7.10 (1 H, d, *J* 10 Hz), 8.25 (1 H, dd, *J* 10 and 3 Hz), and 8.46 (1 H, d, *J* 3 Hz); *m/e* 302 (M^+) and 285 (base).

Ethyl α-chloroacetoacetate 2,4-dinitrophenylhydrazone (0.2 g, 0.58 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) gave 1-(2,4-*dinitrophenyl*)-4-*ethoxycarbonyl*-3-*methyl*-4,4a,5,-7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11e) (0.180 g, 83%) as a mixture of diastereoisomers, m.p. 140—160 °C; several recrystallisations gave a solid, m.p. 155—163 °C (from dichloromethane–hexane) (Found: C, 54.6; H, 5.0; N, 14.9. $C_{17}H_{18}N_4O_6$ requires C, 54.5; H, 4.9; N, 15.0%); $\nu_{max.}$ 1 720 and 1 610 cm⁻¹; δ 1.34 (3 H, t, *J* 7 Hz), 2.16 (3 H), 2.45 (1 H, d, *J* 17 Hz), 2.72 (1 H, dd, *J* 17 and 9 Hz), 3.46 (1 H, d, $J_{4,4a}$ 5 Hz, H-4), 3.65 (1 H, m), 4.30 (2 H, dq, *J* 1 and 7 Hz), 5.25 (1 H, d, br, $J_{4a,7a}$ 9.8 Hz, H-7a), 5.83 (1 H, m, H-6), 6.04 (1H, m, H-7), 7.28 (1 H, d, *J* 10 Hz), 8.33 (1 H, dd, *J* 10 and 2.4 Hz), and 8.56 (1 H, d, *J* 2.4 Hz); *m/e* 374 (M^+) and 357 (base).

Ethyl 3-(4-nitrophenylazo)but-2-enoate (0.2 g, 0.76 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) were dissolved in tetrahydrofuran (10 cm³) and the solution was heated under reflux for 2 h. The solvent was removed to give a viscous yellow oil which crystallised when triturated with ethanol; this was 4-*ethoxycarbonyl*-3-*methyl*-1-(4-*nitrophenyl*)-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11f) (0.219 g, 88%), m.p. 113—114 °C (from dichloromethane–hexane) (Found: C, 62.2; H, 6.0; N, 13.0. $C_{17}H_{19}N_3O_4$ requires C, 62.0; H, 5.8; N, 12.8%); $\nu_{max.}$ 1 720 and 1 595 cm⁻¹; δ 1.32 (3 H, t, *J* 7.3 Hz), 2.19 (3 H), 2.46 (1 H, br d, *J* 17 Hz), 2.70 (1 H, br d, *J* 17 Hz), 3.43 (1 H, d, $J_{4,4a}$ 4.9 Hz, H-4), 3.48—3.60 (1 H, m, H-4a), 4.26 (2 H, q, *J* 7.3 Hz), 5.21 (1 H, br d, $J_{4a,7a}$ 9.8 Hz, H-7a), 5.83 (1 H, m, H-6), 5.94 (1 H, m, H-7), 7.22 (2 H, d, *J* 10 Hz), and 8.16 (2 H, d, *J* 10 Hz); *m/e* 329 (M^+, base).

Ethyl 3-(phenylazo)but-2-enoate (0.2 g, 0.92 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) were heated in tetrahydrofuran (10 cm³) under reflux for 18 h. T.l.c. gave 4-*ethoxycarbonyl*-3-*methyl*-1-*phenyl*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11h) as an oil; $\nu_{max.}$ 1 720 and 1 600 cm⁻¹; δ 1.22 (3 H, t, *J* 7.2 Hz), 2.08 (3 H), 2.12 (1 H, dd, *endo*-H-5), 2.68 (1 H, dd, *exo*-H-5), (2.94 1 H, d, H-4), 3.16 (1 H, m, H-4a), 4.18 (2 H, dq, *J* 2.2 and 7.2 Hz, CH_2 of ester), 4.84 (1 H, d, H-7a), 5.87 (2 H, H-6 and H-7), 6.80—6.90 (1 H, m, *para*-H of phenyl), and 7.17—7.30 (4 H, m). The following coupling constants were obtained by decoupling experiments: $J_{4.4a}$ 7.4 Hz, $J_{4a,5\text{-}endo}$ 2.8 Hz, $J_{4a,5\text{-}exo}$ 7.8 Hz, $J_{4a,7a}$ 9.8 Hz, and $J_{5,gem}$ 17.2 Hz; *m/e* 284 (M^+), 255, 239, 211, and 77 (base).

When the above experiment was conducted at 20 °C the yield of the product was 13%, and it consisted of a mixture of (11h) and an isomer in the ratio 3 : 2. The following signals were distinguished as being those derived from the isomer: δ 1.26 (3 H, t, *J* 7.2 Hz), 2.16 (3 H), 3.60 (1 H, m), 5.14 (1 H, d), and 5.73 (2 H); other signals were superimposed. The spectrum simplified to that of a single isomer when this product was heated to 120—150 °C for 10 min or when it was dissolved in tetrahydrofuran containing a few drops of concentrated hydrochloric acid.

The ester (11h) was hydrolysed by heating under reflux with aqueous sodium hydroxide (20%) for 2 h. The reaction mixture was acidified and the organic product was extracted with ethyl acetate. Column chromatography (silica; chloroform) gave 3-*methyl*-1-*phenyl*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (11j) (52%) as an oil; $\nu_{max.}$ 3 200, 1 595, and 1 505 cm⁻¹; δ 1.90 (1 H, dd, *J* 15.9 and 7.3 Hz), 2.02 (3 H, s, with 1 H, m, superimposed), 2.10 (1 H, dd, *J* 15.9 and 4.9 Hz), 2.60—2.74 (2 H, m), 4.77 (1 H, br), 5.87 (2 H), 6.78—6.88 (1 H, m), and 7.20—7.30 (4 H, m); *m/e* 212 (M^+, base), and 197. A specimen of the same adduct (11j) was prepared independently from 2-(phenylazo)propene (0.084 g, 0.57 mmol) and cyclopentadiene (1 cm³, 12.2 mmol) at 20 °C. After 20 h the adduct was isolated (14%) as an oil, with spectra identical to those described above.

The pyridazine (11j) (0.289 g, 1.4 mmol) in methanol (30 cm³) was hydrogenated over Pd–C to give 3-*methyl*-1-*phenyl*-4,4a,5,6,7,7a-*hexahydro*-1H-*cyclopenta*[c]*pyridazine* (17) (0.285 g, 98%), m.p. 38 °C (from pentane) (Found: C, 78.7; H, 8.5; N, 13.3. $C_{14}H_{18}N_2$ requires C, 78.5; H, 8.5; N, 13.1%); $\nu_{max.}$ 1 600 and 1 505 cm⁻¹; δ 1.30—1.90 (7 H, m), 2.04 (3 H), 2.10—2.30 (2 H, m), 4.04 (1 H, m), 6.82 (1 H, m), and 7.20—7.30 (4 H, m); *m/e* 214 (M^+) and 171 (base).

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) and 2,3-dimethylbutadiene (0.6 cm³, 5.3 mmol) gave 1-(2,4-*dinitrophenyl*)-6-*methyl*-3-*phenyl*-6-α-*methylvinyl*-1,4,5,6-*tetrahydropyridazine* (12) (0.134 g, 67%), m.p. 210—211 °C (decomp.) (from ethanol–ethyl acetate) (Found: C, 62.9; H, 5.1; N, 14.9. $C_{20}H_{20}N_4O_4$ requires C, 63.1; H, 5.3; N, 14.7%); $\nu_{max.}$ 1 603 cm⁻¹; δ 1.64 (3 H), 1.83 (3 H), 1.85—1.95 (1 H, m), 2.20—2.33 (1 H, m), 2.40—2.75 (2 H, m), 4.92 (1 H), 5.10 (1 H), 7.30—7.46 (3 H, m), 7.40 (1 H, d, *J* 10 Hz), 7.50—7.58 (2 H, m), 8.17 (1 H, dd, *J* 10 and 3 Hz), and 8.56 (1 H, d, *J* 3 Hz); *m/e* 380 (M^+, base).

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) and furan (5 cm³) gave 1-(2,4-*dinitrophenyl*)-3-*phenyl*-1,4,4a,7a-*tetrahydrofuro*[3,2-c]*pyridazine* (13a) (0.171 g, 89%), m.p. 177—179 °C (from ethanol) (Found: C, 58.9; H, 3.7; N, 15.4. $C_{18}H_{14}N_4O_5$ requires C, 59.0; H, 3.9; N, 15.3%); $\nu_{max.}$ 1 610 cm⁻¹; δ (100 MHz) 2.54

(1 H, dd, *J* 14 and 4 Hz, H-4), 3.44 (1 H, dd, *J* 14 and 4 Hz, H-4), 5.09 (1 H, br, H-7), 5.29—5.62 (2 H, m, H-4a and H-7a), 6.45 (1 H, br, H-6), 7.24 (1 H, d, *J* 9 Hz), 7.32—7.48 (3 H, m), 7.50—7.70 (2 H, m), 8.30 (1 H, dd, *J* 9 and 3 Hz), and 8.56 (1 H, d, *J* 3 Hz); *m/e* 366 (M^+).

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) and 2,5-dimethylfuran (0.56 cm³, 5.3 mmol) gave 1-(2,4-*dinitrophenyl*)-4a,6-*dimethyl*-3-*phenyl*-1,4,4a,7a-*tetrahydrofuro*[3,2-c]*pyridazine* (13b) (0.180 g, 87%), m.p. 190—194 °C (from ethanol) (Found: C, 61.0; H, 4.5; N, 14.2. $C_{20}H_{18}N_4O_5$ requires C, 60.9; H, 4.6; N, 14.2%); $\nu_{max.}$ 1 600 cm^{-1}; δ (100 MHz) 1.68 (6 H, Me-4a and Me-6), 2,39 (1 H, d, *J* 14 Hz, H-4), 3.38 (1 H, d, *J* 14 Hz, H-4), 4.72 (1 H, br, H-7), 4.90 (1 H, d, *J* 2 Hz, br, H-7a), 7.24 (1 H, d, *J* 9 Hz), 7.30—7.45 (3 H, m), 7.50—7.74 (2 H, m), 8.31 (1 H, dd, *J* 9 and 3 H), and 8.59 (1 H, d, *J* 3 Hz); *m/e* 394 (M^+, base).

Chloroacetone 2,4-dinitrophenylhydrazone (0.2 g, 0.73 mmol) and furan (5 cm³) gave 1-(2,4-*dinitrophenyl*)-3-*methyl*-1,4,4a,7a-*tetrahydrofuro*[3,2-c]*pyridazine* (13c) (0.05 g, 22%), m.p. 192 °C (decomp.) (from ethanol) (Found: C, 51.1; H, 3.8; N, 18.1. $C_{13}H_{12}N_4O_5$ requires C, 51.3; H, 4.0; N, 18.4%); $\nu_{max.}$ 1 608 cm^{-1}; δ (100 MHz) 2.10 (3 H), 2.36 (1 H, dd, *J* 14 and 2.5 Hz, H-4), 2.76 (1 H, dd, *J* 14 and 2 Hz, H-4), 5.08 (1 H, m, H-7), 5.27—5.38 (2 H, m, H-4a and H-7a), 6.51 (1 H, br, H-6), 7.17 (1 H, d, *J* 9 Hz), 8.28 (1 H, dd, *J* 9 and 3 Hz), and 8.57 (1 H, d, *J* 3 Hz); *m/e* 304 (M^+).

Chloroacetone 2,4-dinitrophenylhydrazone (0.2 g, 0.73 mmol) and 6,6-dimethylfulvene (1 cm³, 8.4 mmol) gave 1-(2,4-*dinitrophenyl*)-3-*methyl*-5-*prop*-2-*ylidene*-4,4a,5,7a-*tetrahydro*-1H-*cyclopenta*[c]*pyridazine* (14) (0.171 g, 68%), m.p. 175—178 °C (decomp.) (from chloroform–hexane) (Found: C, 59.5; H, 5.4; N, 16.6. $C_{17}H_{18}N_4O_4$ requires C, 59.6; H, 5.3; N, 16.4%); $\nu_{max.}$ 1 610 cm^{-2}; δ 1.82 (6 H) 2.03 (3 H), 2.16 (1 H, dd, *J* 14.7 and 5 Hz, H-4), 2.38 (1 H, dd, *J* 14.7 and 7.3 Hz, H-4), 3.54 (1 H, m, H-4a), 5.17 (1 H, d, *J* 7.6 Hz, br, H-7a), 5.82 (1 H, d, *J* 4.9 Hz), 6.65 (1 H, d, *J* 6.2 Hz, further split), 7.24 (1 H, d, *J* 9 Hz), 8.30 (1 H, dd, *J* 9 and 2.4 Hz), and 8.53 (1 H, d, *J* 2.4 Hz); *m/e* 342 (M^+).

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.2 g, 0.53 mmol) and 1-methoxy-3-trimethylsilyloxybutadiene [33] (0.8 g, 4.7 mmol) gave trans-6-*methoxy*-1-*phenylhex*-5-*ene*-1,4-*dione* 1-(2,4-*dinitrophenylhydrazone*) (15) (0.068 g, 32%), m.p. 136—139 °C (from ethanol) (Found: C, 57.5; H, 4.5; N, 13.9. $C_{19}H_{18}N_4O_6$ requires C, 57.3; H, 4.6; N, 14.1%); $\nu_{max.}$ 3 310 (NH), 1 680 (C=O), and 1 605 cm^{-1}; δ (100 MHz) 2.80—2.96 (2 H, m), 3.08—3.26 (2 H, m), 3.65 (3 H), 5.53 (1 H, d, *J* 12.5 Hz), 7.36—7.48 (3 H, m), 7.58 (1 H, d, *J* 12.5 Hz), 7.74—7.86 (2 H, m), 8.02 (1 H, d, *J* 9 Hz), 8.28 (1 H, dd, *J* 9 and 3 Hz), and 9.13 (1 H, d, *J* 3 Hz); *m/e* 398 (M^+) and 130 (base).

α-Bromoacetophenone 2,4-dinitrophenylhydrazone (0.719 g, 1.9 mmol) and cyclopentane (17.5 cm³, 0.20 mol) in tetrahydrofuran (100 cm³) gave, with anhydrous sodium carbonate (1 g), 1-(2,4-*dinitrophenyl*)-3-*phenyl*-4,4a,5,6,-7,7a-*hexahydro*-1H-*cyclopenta*[c]*pyridazine* (16) (0.141 g, 20%), m.p. 162—163 °C (from ethanol) (Found: C, 62.5; H, 4.9; N, 15.2. $C_{19}H_{18}N_4O_4$ requires C, 62.3; H, 5.0; N, 15.3%); $\nu_{max.}$ 1 600 cm^{-1}; δ 1.56—2.10 (5 H, m), 2.20—2.44 (2 H, m, containing a dd, *J* 16.7 and 8.3 Hz), 2.50—2.65 (1 H, m), 2.76 (1 H, dd, *J* 16.7 and 6.0 Hz), 4.27 (1 H, m), 7.22 (1 H, d, *J* 9.8 Hz), 7.34—7.47 (3 H, m), 7.57—7.70 (2 H, m), 8.26 (1 H, dd, *J* 9.8 and 2.4 Hz), and 8.50 (1 H, d, *J* 2.4 Hz); *m/e* 366 (M^+) and 135 (base). The azoalkene dimer (10) (0.848 g, 75%) was also isolated.

Chloroacetone 2,4-dinitrophenylhydrazone (0.2 g, 0.73 mmol) and α-morpholinosytrene (0.139 g, 0.74 mmol) gave 1-*methyl*-4-*phenylbutane*-1,4-*dione* 1-(2,4-*dinitrophenylhydrazone*) (21) (0.132 g, 51%), m.p. 197—198 °C (from chloroform) (Found: C, 57.2; H, 4.3; N, 15.9. $C_{17}H_{16}N_4O_5$ requires C, 57.3; H, 4.5; N, 15.7%); $\nu_{max.}$ 3 300 (NH), 1 670 (CO), and 1 615 cm^{-1}; δ 2.15 (3 H), 2.96 (2 H, t, *J* 7 Hz), 3.36 (2 H, t, *J* 7 Hz), 7.36 (1 H, d, *J* 9.8 Hz), 7.50—7.62 (3 H, m), 7.95 (1 H, dd, *J* 9.8 and 3 Hz), 8.00—8.10 (2 H, m), and 9.06 (1 H, d, *J* 3 Hz); *m/e* 356 (M^+), 321, and 105 (base).

We thank the S.R.C. for a Research Studentship (to R. F.), and Dr. J. M. Behan for carrying out the molecular-orbital calculations.

[8/269 *Received*, 16*th February*, 1978]

REFERENCES

[1] Preliminary communication, R. Faragher and T. L. Gilchrist, *J.C.S. Chem. Comm.*, 1976, 581.
[2] J. Hamer and M. Ahmed in ' 1,4 Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 419; B. T. Cullis, *ibid.*, p. 143.
[3] G. W. Kirby and J. G. Sweeny, *J.C.S. Chem. Comm.*, 1973, 704; G. W. Kirby and J. W. M. Mackinnon, *ibid.*, 1977, 23.
[4] T. L. Gilchrist, M. E. Peek, and C. W. Rees, *J.C.S. Chem. Comm.*, 1975, 913, 914; T. J. Gilchrist, C. J. Harris, F. D. King, M. E. Peek, and C. W. Rees, *J.C.S. Perkin I*, 1976, 2161.
[5] P. Horsewood and G. W. Kirby, *Chem. Comm.*, 1971, 1139; G. W. Kirby, *Chem. Soc. Rev.*, 1977, **6**, 1.
[6] R. Faragher and T. L. Gilchrist, *J.C.S. Perkin I*, 1977, 1196.
[7] G. Just and W. Zehetner, *Chem. Comm.*, 1971, 81.
[8] K. N. Zelenin and Z. M. Matveeva, *Zhur. org. Khim.*, 1968, **4**, 532; 1970, **6**, 717; *Doklady Akad. Nauk S.S.S.R.*, 1969, **184**, 1105; K. N. Zelenin, Z. M. Matveeva, and L. Y. Ermolaeva, *Zhur. org. Khim.*, 1970, **6**, 723; K. N. Zelenin, V. A. Nikitin, N. M. Anodina, and Z. M. Matveeva, *ibid.*, 1972, **8**, 1438; K. N. Zelenin, V. A. Nikitin, and N. M. Anodina, *Khim. geterotsikl. Soedinenii*, 1973, 124 (*Chem. Abs.*, 1973, **78**, 110 399); L. Cagliotti, G. Rosini, P. Tundo, and A. Vigevani, *Tetrahedron Letters*, 1970, 2349; P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, *J.C.S. Perkin I*, 1972, 2611; P. M. Collins, J. R. Hurford, and W. G. Overend, *ibid.*, 1975, 2178.
[9] W. Höbold, U. Prietz, and W. Pritzkow, *J. prakt. Chem.*, 1968, **311**, 260; K. Wieser and A. Berndt, *Angew. Chem. Internat. Edn.*, 1975, **14**, 70.
[10] M. Angermann, J. Beger, G. Collin, A. Ebenroth, R. Hellmig, H. Lunkwitz, P. Pabst, U. Prietz, W. Pritzkow, H. Schaefer, R. Siedler, and R. Weller, *Wiss. Z. tech. Hochschule Chem. Leuna-Merseburg*, 1966, **8**, 187.
[11] D. Y. Curtin and E. W. Tristram, *J. Amer. Chem. Soc.*, 1950, **72**, 5238.
[12] U. M. Kempe, T. K. Das Gupta, K. Blatt, P. Gygax, D. Felix, and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 2187.
[13] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
[14] G. Desimoni and G. Tacconi, *Chem. Rev.*, 1975, **75**, 651.
[15] R. Faragher and T. L. Gilchrist, following paper.
[16] D. Mackay, J. A. Campbell, and C. P. R. Jennison, *Canad. J. Chem.*, 1970, **48**, 81; J. A. Campbell, D. Mackay, and T. D. Sauer, *ibid.*, 1972, **50**, 371; G. W. Kirby and J. W. M. Mackinnon, *J.C.S. Chem. Comm.*, 1977, 23.
[17] H. G. Viehe, R. Merényi, E. Francotte, M. Van Meerssche, G. Germain, J. P. Declercq, and J. Bodart-Gilmont, *J. Amer. Chem. Soc.*, 1977, **99**, 2340.
[18] S. Sommer, *Tetrahedron Letters*, 1977, 117.
[19] S. Itô and I. Saito, *Tetrahedron Letters*, 1977, 1203.
[20] H. Korten and R. Scholl, *Ber.*, 1901, **34**, 1901.
[21] H. Brintzinger and R. Titzmann, *Chem. Ber.*, 1952, **85**, 344.
[22] R. Biela, I. Hahnemann, H. Panovsky, and W. Pritzkow, *J. prakt. Chem.*, 1966, **33**, 282.
[23] A. Arcoria, S. Fisichella, E. Maccarone, and G. Scarlata, *J. Heterocyclic Chem.*, 1975, **12**, 215.

[24] S. Brodka and H. Simon, *Annalen*, 1971, **745**, 193.
[25] G. Rosini and S. Cacchi, *J. Org. Chem.*, 1972, **37**, 1856.
[26] H. Simon and W. Moldenhauer, *Chem. Ber.*, 1968, **101**, 2124.
[27] J. van Alphen, *Rec. Trav. chim.*, 1945, **64**, 109.
[28] J. van Alphen, *Rec. Trav. chim.*, 1945, **64**, 305.
[29] G. D. Johnson, *J. Amer. Chem. Soc.*, 1951, **73**, 5888.
[30] C. Bülow and F. Seidel, *Annalen*, 1924, **439**, 49.
[31] A. Ross and R. N. Ring, *J. Org. Chem.*, 1961, **26**, 579.
[32] This compound was prepared by the method described by A. Dondoni, G. Rossini, G. Mossa, and L. Caglioti, *J. Chem. Soc.* (*B*), 1968, 1404.
[33] S. Danishefsky and A. Kitahara, *J. Amer. Chem. Soc.*, 1974, **96**, 7807.