The Cycloaddition of α-Nitrosostyrenes to Olefins. Investigations of the Scope and Mechanism of the Reaction

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Cycloaddition of α-nitrosostyrene (1a) to several substituted styrenes is shown to give 3-phenyl-5,6-dihydro-4*H*-1,2-oxazines (2) in moderate yield. Reactions with 4-nitro-α-nitrosostyrene (1b) give better yields of the corresponding adducts (3). The preferred conformations of the adducts are deduced from their n.m.r. spectra. The observed regio- and stereo-selectivities of the additions are interpreted in terms of a one-step addition in which the olefins act as the donor components.

The first example of a formal 1,3-dipolar addition of a vinyl nitroso compound is provided by the formation of the nitrone (5) as a minor product of the reaction of α-nitrosostyrene with 2-methoxypropene. The relative yield of this nitrone is not increased by the change to a more polar solvent, nor by the use of α-bromoacetophenone *anti*-oxime in place of the usual *syn* isomer as the precursor of α-nitrosostyrene. It is suggested that this, and other minor products (4) isolated from the cycloadditions, may be formed because of steric inhibition of the usual Diels–Alder-type process.

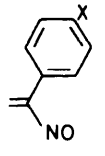
α-Nitrosostyrene (1a) has been suggested as a likely intermediate in the reactions of α-halogenoacetophenone oximes with bases.[1,2] We have shown that if the intermediate is generated slowly in an aprotic solvent by the use of a heterogeneous base (sodium carbonate), it can be intercepted by cycloaddition with nucleophilic dienes.[2] The products are 5,6-dihydro-4*H*-1,2-oxazines (2) and are thus formally the result of a cycloaddition in which the α-nitrosostyrene has acted as a heterodiene. No cycloaddition was observed with simple alkenes like cyclopentene, but indene did form an adduct in low yield.

We have carried out further reactions of this type in order to determine the scope and limitations of the cycloaddition reaction between α-nitrosostyrene and olefins, and to investigate the regio- and stereo-chemistry of the additions. We have also explored the analogous reactions of 4-nitro-α-nitrosostyrene (1b) which we expected to be a more electrophilic reagent than (1a).

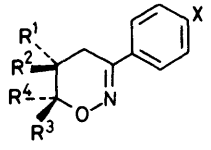
Reactions of α-Nitrosostyrene (1a).—The additions were carried out by stirring a solution of α-chloroacetophenone oxime and an excess (5—10 mol ratio olefin : oxime) of the olefin in dichloromethane at room temperature with sodium carbonate. After 24 h the solvent and the excess of the olefin were removed and the products were examined by n.m.r. spectroscopy. They were then isolated, usually by means of preparative layer chromatography (p.l.c.). The adducts (2a—f) formed from conjugated olefins were isolated in the yields shown in Table 1. No adducts could be detected with (*Z*)-stilbene or with (*Z*)-1-phenylpropene. Cyclohexene gave a trace of an adduct (2g) which was shown (n.m.r.) to be identical with the product of hydrogenation of the cyclohexadiene adduct (2f).

Reactions of 4-Nitro-α-nitrosostyrene (1b).—Cycloadditions were carried out in the same way as for α-nitrosostyrene, using α-bromo-4-nitroacetophenone oxime [4] as the precursor. The oxazines (3) were isolated in the yields shown in Table 2. The adducts were invariably isolated in higher yields than in the comparable reactions with α-nitrosostyrene, and even the simple alkene oct-1-ene gave adducts in moderate yield (40%). No adduct could be detected from (*Z*)-stilbene or from a conjugated alkyne, 1-phenylpropyne.

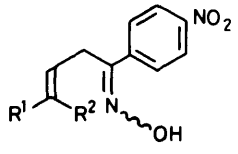
In the reactions of styrene, α-methylstyrene, and 1,1-diphenylethylene, other minor products were isolated. The product from addition to 1,1-diphenylethylene, which was isolated in 10% yield, was characterised and was identified as



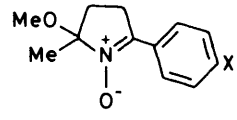
(1) a; X = H
b; X = NO_2



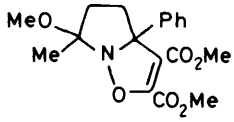
(2) X = H
(3) X = NO_2



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



(5) a; X = H
b; X = NO_2



(6)

Table 1. 3-Phenyl-5,6-dihydro-4*H*-1,2-oxazines (2) from olefins and α-nitrosostyrene

Olefin	Oxazine	R^1	R^2	R^3	R^4	Yield (%) [a]
Styrene	(2a)	H	H	Ph	H	42
α-Methylstyrene	(2b)	H	H	Ph	Me	26
(*E*)-1-Phenylpropene	(2c)	Me	H	Ph	H	26 [b]
	(2d)	Ph	H	Me	H	
(*E*)-Stilbene	(2e)	Ph	H	Ph	H	5
Cyclohexa-1,3-diene	(2f)	H	$-[CH_2]_2CH{=}CH-$		H	69 [c]
Cyclohexene	(2g)	H	$-[CH_2]_4-$		H	Trace

[a] Isolated yields, reproducible within 2—3%. [b] Isomer ratio by n.m.r. is (2c) : (2d) 69 : 31. [c] Lit.,[3] 46%.

Table 2. 3-Aryl-5,6-dihydro-4*H*-1,2-oxazines (3) from olefins and 4-nitro-α-nitrosostyrene

Olefin	Oxazine	R^1	R^2	R^3	R^4	Yield (%)
Styrene	(3a)	H	H	Ph	H	88
α-Methylstyrene	(3b)	H	H	Ph	Me	83
1,1-Diphenylethylene	(3c)	H	H	Ph	Ph	56
(*E*)-1-Phenylpropene	(3d)	Me	H	Ph	H	90 [a]
	(3e)	Ph	H	Me	H	
(*Z*)-1-Phenylpropene	(3f)	H	Me	Ph	H	2.5
(*E*)-1-(4-Methoxyphenyl)propene	(3g)	Me	H	C_6H_4OMe-4	H	80 [b]
	(3h)	C_6H_4OMe-4	H	Me	H	
(*Z*)-1-(4-Methoxyphenyl)propene	(3i)	H	Me	C_6H_4OMe-4	H	18 [c]
(*E*)-Stilbene	(3j)	Ph	H	Ph	H	57
Oct-1-ene	(3k)	H	H	C_6H_{13}	H	40 [d]
	(3l)	C_6H_{13}	H	H	H	

[a] Isomer ratio by n.m.r. is (3d) : (3e) 56 : 44. [b] Isomer ratio is (3g) : (3h) 87.5 : 12.5. [c] Olefin contains *ca.* 1% *E*-isomer; compound (3g) (8%) was also isolated. [d] Isomer ratio is (3k) : (3l) 85 : 15.

Table 3. Chemical shifts and coupling constants for 6-H for some of the oxazines (2) and (3)

Starting olefin	Oxazine	δ (6-H)	$J_{5,6}$ (Hz)
Styrene	(2a)	4.87	10.1, 2.9
	(3a)	4.90	10.1, 2.9
(*E*)-1-Phenylpropene	(2c)	4.38	9.1
	(2d)	3.95	9.2
	(3d)	4.44	9.5
	(3e)	4.04	*a*
(*E*)-1-(4-Methoxyphenyl)-propene	(3g)	4.38	9.5
(*E*)-Stilbene	(2e)	4.84	11.0
	(3j)	4.88	9.7

[a] Multiplet, not resolved.

the oxime (4c); those from styrene and from α-methylstyrene are assigned the analogous structures (4a) and (4b) {(*E*/*Z*) mixture} on the basis of their n.m.r. spectra. It was established by a control experiment that the oxazine (3c) was not converted into the oxime (4c) under the reaction conditions; hence, the oximes appear to be formed in independent reactions.

The effect of change of solvent on the ratio of the products (3c) : (4c) was also investigated. The reaction was repeated in three other solvents: benzene, acetonitrile, and nitromethane. Although the overall yields of adducts were much lower in acetonitrile and in nitromethane, there was no significant solvent effect on the isomer ratios, which varied between 3.4 : 1 (benzene) and 4.9 : 1 (dichloromethane).

Several of the reactions summarised in Table 2 gave mixtures of regioisomeric oxazines, but in only one case, that of the addition to (*Z*)-1-(4-methoxyphenyl)propene, were mixtures of stereoisomers detected. This olefin was prepared by the catalytic hydrogenation of the corresponding alkyne. None of the *E*-isomer could be detected by ^{1}H n.m.r. spectroscopy, but g.l.c. revealed the presence of *ca.* 1% *E*-isomer in the olefin. The reaction was performed with a 5-mol excess of the olefin and it is clear that the *E*-isomer would add preferentially: nevertheless, the amount of adduct (3g) which was isolated (8%) is more than can be accounted for from the amount of *E*-isomer initially present.

Structures of the Oxazines (2) *and* (3).—The 220-MHz ^{1}H n.m.r. spectra of the adducts proved to be invaluable in assigning structures and in analysing mixtures of regio- and stereo-isomers. The nature and positions of the signals for the

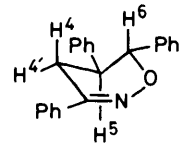


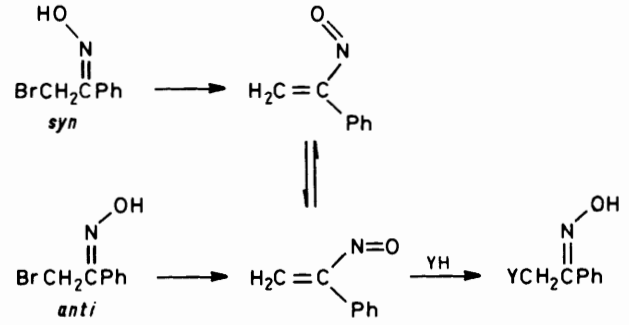
Figure. Proposed conformation of the oxazine (2e). Coupling constants are $J_{4,4'}$ −18.5, $J_{4,5}$ 11.0, $J_{4,5'}$ 6.0, and $J_{5,6}$ 11.0 Hz

6-H atoms of the oxazines are particularly diagnostic. Thus, 6-H in the adduct (3d) appears at δ 4.44, whereas in the regioisomer (3e) it is at δ 4.04. In (3d) the hydrogen atom is benzylic and is thus deshielded relative to that in (3e). 6-H in compound (3d) appears as a doublet (*J* 9.5 Hz), which is consistent with a conformation for the compound in which 5-H and 6-H occupy axial positions. This was also found to be the case for other adducts of this type: the relevant chemical shifts and coupling constants for 6-H are summarised in Table 3.

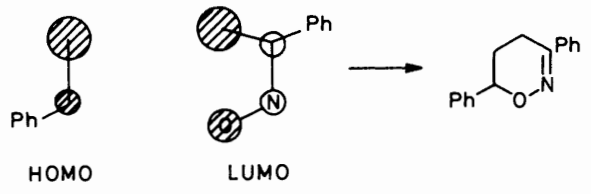
A complete analysis of the signals in the (*E*)-stilbene adduct (2e) was carried out. The coupling constants are consistent with a half-chair conformation for the oxazine (Figure) in which the phenyl groups at C-5 and C-6 occupy equatorial positions. Coupling constants for the other oxazines in Table 3 are also consistent with analogous conformations for these compounds.

Two adducts of *Z*-olefins were isolated, *viz.* the oxazines (3f) and (3i). The signals for 6-H in these adducts are at δ 5.07 and 5.03, respectively, and, in contrast to the adducts in Table 3, show very small coupling constants of *ca.* 2 Hz. These are consistent with an axial–equatorial arrangement of 5-H and 6-H. Since the other coupling constants in the molecules indicate that 5-H is axial, this means that in these adducts 6-H is equatorial and the aryl group at C-6 occupies an axial position. The *cis*-5,6-disubstituted adducts are thus characterised by two features: the larger chemical shifts and the smaller coupling constants of 6-H relative to those in the *trans*-disubstituted adducts.

Addition of α-*Nitrosostyrene* (1a) *to* 2-*Methoxypropene*.—α-Nitrosostyrene (1a) has been shown to undergo cycloaddition reactions, not only with dienes and styrene derivatives, but also with electron-rich olefins: thus, enamines [2,5] and some enol ethers [6] have been shown to form oxazines in good yield. Addition of α-nitrosostyrene (from α-chloroacetophenone oxime) to 2-methoxypropene gave, as the major product, the expected oxazine (2; $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Me$), but there was also a second (isomeric) product, which was isolated in 10% yield. This was shown to



Scheme 1.



Scheme 2.

be the nitrone (5a) on the basis of its n.m.r. spectrum and by the formation of a cycloadduct (6) with dimethyl acetylenedicarboxylate. The isolated yield of the nitrone (5a) was not increased when the reaction was carried out in a more polar solvent (acetonitrile). There was no interconversion of compounds (2h) and (5a) under the reaction conditions.

4-Nitro-α-nitrosostyrene (1b) and 2-methoxypropene gave an analogous pair of adducts, the oxazine (3m; $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Me$) (81%) and the nitrone (5b) (11%).

The α-nitrosostyrenes have thus formally acted as 1,3-dipoles in the formation of the nitrones (5). Nitrones have not previously been observed as products of addition of vinyl nitroso compounds, but there are examples of an analogous mode of cycloaddition of vinylazo compounds.[7]

It has been established that α-halogenoacetophenone oximes, as formed from the α-halogenoketones, are in the thermodynamically favoured *syn*-configuration, but that in reactions with nucleophilic bases, the substitution products have the *anti*-configuration.[8] This has been ascribed to preferential addition to α-nitrosostyrene in its *transoid* form (Scheme 1).[1] We therefore considered the possibility that the nitrones (5) resulted from nucleophilic addition or cycloaddition of the enol ether to the *transoid* form of the α-nitrosostyrene. If rotation about the C–N bond of α-nitrosostyrene were slow, as seemed reasonable on the basis of calculations on the structures of vinyl nitroso compounds,[9] then the generation of the intermediate from an α-halogenoacetophenone *anti*-oxime might give the nitrone (5) as the major product. Both α-bromoacetophenone *syn*- and *anti*-oximes have been prepared and fully characterised.[8] We repeated the preparations of the *syn*- and *anti*-oximes and compared the products of their reaction with 2-methoxypropene and sodium carbonate under identical conditions. There was no detectable difference in the ratio of the products (2h) and (5a) from the two oximes. We therefore conclude that the configuration of the nitrosostyrene (1a), as initially generated from the oximes, is not significant in determining the types of products: rotation about the C–N bond must therefore occur *before* the cycloadducts are formed.

Reaction Mechanisms.—The following general features concerning the formation of the oxazines (2) and (3) emerge from these reactions. (i) Olefins which give the higher yields are those bearing conjugated aryl or vinyl groups, and those with electron-releasing substituents; that is, those with a high-lying, filled molecular orbital. (ii) The incorporation of an electron-withdrawing nitro group into the α-nitrosostyrene increases the yields of adducts. (iii) The regioselectivity of the addition is that which would be expected for a reaction controlled primarily by frontier orbital interactions, with the olefin as the donor component;[10] that is, the major regioisomer is that in which the terminal atom of the olefin bearing the higher HOMO coefficient interacts with the terminal carbon atom of the nitrosostyrene, which in the LUMO bears the higher orbital coefficient.[2] This is illustrated in Scheme 2 for the addition to styrene. (iv) The cycloadditions are highly stereoselective. In only one case, the addition of 4-nitro-α-nitrosostyrene (1b) to (*Z*)-1-(4-methoxyphenyl)propene, was there evidence for loss of stereoselectivity, and here the reaction is complicated by the much more ready addition of the *E*-isomer present as an impurity.

These results are consistent with a description of the reaction as a Diels–Alder process with ' inverse electron demand ', that is, one in which the heterodiene is the electron-deficient component.[10] There is no indication of a long-lived dipolar intermediate in the reaction, so the process is probably best regarded as a one-step reaction through an unsymmetrical transition state in which the formation of the C–O bond lags behind the formation of the C–C bond. The minor products (4) and (5) which were isolated were all formed in cases where dipolar intermediates would be particularly well stabilised, but there was no evidence for an increase in these side-products in more polar solvents. The reasons for their formation are, therefore, open to speculation. Possibly, those olefins which bear two groups at the terminal carbon disfavour the transition state for oxazine formation owing to steric interaction, and an alternative mode of addition, involving the *transoid* conformation of the nitrosostyrene, is then able to compete.

Experimental

I.r. spectra were recorded for KBr discs on a Perkin-Elmer 125 spectrophotometer. ^1H N.m.r. spectra were recorded using a Perkin-Elmer R34 spectrometer, operating at 220 MHz, and deuteriochloroform as solvent. Mass spectra were recorded on an A.E.I. MS12 instrument at 70 eV using a direct insertion probe. P.l.c. was carried out on plates coated with Kieselgel PF_{254} (Merck).

α-Bromo-4-nitroacetophenone Oxime.—This was prepared by a modification of the literature [4] method. α-Bromo-4-nitroacetophenone (14 g, 57 mmol) was dissolved in methanol (400 cm^3) and a solution of hydroxylamine sulphate (14.8 g, 90 mmol) in water (50 cm^3) was added. The mixture was stirred at room temperature and the reaction monitored by t.l.c. (100% dichloromethane)—after 4.5 h, consumption of starting materials was complete. The mixture was poured onto water (1 500 cm^3) and the resulting precipitate was recrystallised to give the oxime (10.5 g, 71%), m.p. 125—127 °C (from dichloromethane–hexane) (lit.,[4] 120—122 °C); δ 4.43 (2 H, CH_2Br), 7.88 (2 H, d, 2- and 6-H), 8.27 (2 H, d, 3- and 5-H), and 8.38 (1 H, OH).

(*Z*)-1-*Phenylpropene.*[11]—This olefin was prepared stereospecifically by reduction of 1-phenylpropyne [12] using ' Nickel-P2 ' catalyst [13] with ethylenediamine. Nickel acetate tetrahydrate (0.75 g, 3 mmol) was dissolved in dry ethanol (40 cm^3) and the flask was purged with hydrogen. A solution of

sodium borohydride (0.114 g, 3 mmol) in ethanol (10 cm^3) was added to give a fine black precipitate of ' Nickel-P2 ' catalyst. Ethylenediamine (0.5 cm^3, 0.7 mmol) and 1-phenylpropyne (4.64 g, 40 mmol) were then added. The mixture was stirred and the uptake of hydrogen commenced immediately and continued at a steady rate for 1 h. The mixture was filtered through charcoal and then through Celite. Water (60 cm^3) was added to the filtrate which was then extracted with pentane (3 × 50 cm^3). The combined organic extracts were washed with water and dried (Na_2SO_4). The pentane was removed at atmospheric pressure and the residue was microdistilled at reduced pressure to give (*Z*)-1-phenylpropene (3.5 g, 74%), b.p. 90 °C at 75 mmHg (lit.,[14] 96 °C at 80 mmHg); the ^1H n.m.r. spectrum of the product indicated that it contained no *E*-isomer and was the pure *Z*-olefin; δ 1.87 (3 H, dd, Me), 5.76 (1 H, m, 2-H), 6.43 (1 H, d, 1-H), and 7.1—7.4 (5 H, m, Ph).

(Z)-1-(4-*Methoxyphenyl*)*propene*.—Stereospecific reduction using ' Nickel-P2 ' catalyst was also used in this preparation. Nickel acetate tetrahydrate (1.5 g, 6 mmol) was dissolved in dry ethanol (100 cm^3) and the flask was purged with hydrogen. A solution of sodium borohydride (0.23 g, 6 mmol) in ethanol (25 cm^3) was added to give a fine precipitate of the catalyst. Ethylenediamine (1 cm^3, 1.4 mmol) and 1-(4-methoxyphenyl)-propyne [15] (9 g, 60 mmol) were then added to the stirred mixture. Uptake of hydrogen soon commenced and continued at a steady rate for 4 h. The mixture was filtered, water (100 cm^3) was added to the filtrate, and the solution was extracted with pentane (3 × 100 cm^3). The combined organic extracts were dried (Na_2SO_4) and the pentane was removed at atmospheric pressure. The residual liquid was fractionally distilled under reduced pressure to give the title *Z*-alkene (8 g, 87%), b.p. 125—128 °C at 12—15 mmHg (lit.,[16] 88—90 °C at 5 mmHg); δ 1.89 (3 H, dd, Me), 3.78 (3 H, MeO), 5.70 (1 H, dq, 2-H), 6.38 (1 H, d, 1-H), 6.87 (2 H, d, 3′- and 5′-H), and 7.26 (2 H, d, 2′- and 6′-H). No *E*-isomer could be detected by n.m.r., but analytical g.l.c. showed that there was 1% *E*-isomer in the sample.

Reactions of α-Halogenoacetophenone Oximes with Olefins. —*General procedure*. The α-halogeno-oxime (2 mmol) was dissolved in dry dichloromethane (50 cm^3) and an excess of the substrate was added. Anhydrous sodium carbonate (1.2 g, 11 mmol) was then added and the suspension was stirred for *ca.* 24 h at room temperature. The solution was then filtered through Celite. The solvent was removed and the residue was subjected to chromatography as indicated. The following oxazines were thus prepared.

3,6-*Diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2a). α-Chloroacetophenone oxime (0.339 g, 2 mmol) and styrene (2.08 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1) as developer], the *oxazine* (2a) (0.20 g, 42%), m.p. 160—162 °C (from ethanol–hexane) (Found: C, 80.85; H, 6.5; N, 5.9. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%); $\nu_{max.}$ 1 586 and 1 550 cm^{-1}; δ 2.15—2.41 (2 H, m, 5-H_2), 2.77 (2 H, dt, 4-H_2), 4.87 (1 H, dd, *J* 10.1 and 2.9 Hz, 6-H), 7.35—7.50 (8 H, m, ArH), and 7.72—7.78 (2 H, m, ArH); *m/z* 237 (M^+), 219, 208, 193, 91, and 77 (100%); *m** 182.6 (237 ⟶ 208) and 157.2 (237 ⟶ 193).

6-*Methyl*-3,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2b). α-Chloroacetophenone oxime (0.339 g, 2 mmol) and α-methylstyrene (2.24 g, 19 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)] the *oxazine* (2b) (0.133 g, 26.5%), m.p. 128—129 °C (from ethanol–hexane) (Found: C, 81.05; H, 6.65; N, 5.65. $C_{17}H_{17}NO$ requires C, 81.25; H, 6.8; N, 5.55%); $\nu_{max.}$ 1 590 cm^{-1}; δ 1.59 (3 H, s, 6-Me), 2.00—2.19 and 2.39—2.61 (total 4 H, 2 × m, 4-H_2 and 5-H_2), 7.17—7.45 (8 H, m, ArH), and 7.60 (2 H, m, ArH); *m/z* 251 (M^+), 234, and 77 (100%).

trans-5-*Methyl*-3,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2c) *and its regioisomer* (2d). α-Chloroacetophenone oxime (0.339 g, 2 mmol) and (*E*)-1-phenylpropene (2.24 g, 19 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of two regioisomers, trans-5-*methyl*-3,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2c) and trans-6-*methyl*-3,5-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2d) (0.132 g, 26%). An isomer ratio (2c) : (2d) of 69 : 31 was estimated on comparison of the relevant signals in the ^1H n.m.r. spectrum of the mixture, δ 0.87 [d, 5-Me of (2c)] and 1.17 [d, 6-Me of (2d)]; δ 3.95 [dq, *J* 9.2 and 6.6 Hz, 6-H of (2d)] and 4.38 [d, *J* 9.1 Hz, 6-H of (2c)]. On attempted recrystallisation the major component preferentially crystallised to give the *oxazine* (2c), m.p. 123—124 °C (from ethanol–hexane) (Found: C, 81.0; H, 6.75; N, 5.55. $C_{17}H_{17}NO$ requires C, 81.25; H, 6.8; N, 5.55%); $\nu_{max.}$ 1 595 and 1 590 cm^{-1}; δ 0.87 (3 H, d, *J* 6.6 Hz, 5-Me), 2.26—2.45 (2 H, m, 4- and 5-H), 2.75—2.94 (1 H, m, 4-H), 4.38 (1 H, d, *J* 9.1 Hz, 6-H), 7.38 (8 H, s, ArH), and 7.74 (2 H, m, ArH); *m/z* 251 (M^+).

trans-3,5,6-*Triphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2e). α-Chloroacetophenone oxime (0.339 g, 2 mmol) and (*E*)-stilbene (3 g, 16.7 mmol) gave, on work-up by p.l.c. [chloroform–ethanol (98 : 2)], trans-3,5,6-*triphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2e) (0.031 g, 5%), m.p. 162—165 °C (from ethanol–hexane) (Found: C, 83.9; H, 6.05; N, 4.35. $C_{22}H_{19}NO$ requires C, 84.3; H, 6.1; N, 4.45%); $\nu_{max.}$ 1 590 and 1 585 cm^{-1}; δ 2.85—3.15 (2 H, dq, 4-H_2), 3.31—3.46 (1 H, dt, 5-H), 4.84 (1 H, d, *J* 11.0 Hz, 6-H), and 7.04—7.80 (15 H, m, 3 × Ph); *m/z* 314, 313 (M^+), and 77 (100%).

The signals in the ^1H n.m.r. spectrum attributable to the two C-4 and the C-5 protons were analysed theoretically as an ABX system. This treatment gave the values J_{AB} −18.5, J_{AX} 6.0, and J_{BX} 11.0 Hz, ν_A δ 3.05, ν_B δ 2.93, and ν_X δ 3.38.

3-*Phenyl*-4a,5,6,8a-*tetrahydro*-4H-1,2-*benzoxazine* (2f). α-Chloroacetophenone oxime (0.339 g, 2 mmol) and cyclohexa-1,3-diene (1.6 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], 3-phenyl-4a,5,6,8a-tetrahydro-4*H*-1,2-benzoxazine (2f) (0.294 g, 69%), m.p. 101—102 °C (from ethanol–hexane) (lit.,[3] 103—106 °C) (Found: C, 78.95; H, 6.9; N, 6.7. Calc. for $C_{14}H_{15}NO$: C, 78.95; H, 7.1; N, 6.55%); δ 1.50—1.90 and 2.10—2.30 (total 5 H, m, 4a-H, 5-H_2, and 6-H_2), 2.35 (1 H, dd, 4-H), 2.86 (1 H, dd, 4-H), 4.18 (1 H, m, 8a-H), 5.89 (1 H, m, 7-H), 6.03 (1 H, m, 8-H), 7.34 (3 H, m, ArH), and 7.68 (2 H, m, 2′- and 6′-H); *m/z* 214, 213 (M^+), and 194.

The signals in the ^1H n.m.r. spectrum attributable to the two C-4 protons were analysed theoretically as the AB part of an ABX system. This treatment gave the values J_{AB} −18.3, J_{AX} 8.3, and J_{BX} 3.1 Hz, ν_A δ 2.83, and ν_B δ 2.31.

3-*Phenyl*-4a,5,6,7,8,8a-*hexahydro*-4H-1,2-*benzoxazine* (2g). 3-Phenyl-4a,5,6,8a-tetrahydro-4*H*-1,2-benzoxazine (2f) (0.106 g, 0.5 mmol) was dissolved in dry ethanol (40 ml) containing 5% palladium–charcoal catalyst (0.012 g) and was hydrogenated at atmospheric pressure in a shaken flask for 5 h. The mixture was filtered through Celite, the solvent was removed, and the residue was subjected to p.l.c. [chloroform–ethyl acetate (19 : 1)] which gave 3-*phenyl*-4a,5,6,7,8,8a-*hexahydro*-4H-1,2-*benzoxazine* (2g) (0.084 g, 75%), m.p. 118—119 °C (from ethanol–hexane) (Found: C, 77.8; H, 7.85; N, 6.55. $C_{14}H_{17}NO$ requires C, 78.1; H, 7.95; N, 6.5%); $\nu_{max.}$ 1 585 and 1 560 cm^{-1}; δ 1.25—1.81 (7 H, m, 4a-H, 5-, 6-, and 7-H_2), 1.96—2.19 (2 H, m, 8-H_2), 2.34 (1 H, dd, 4-H), 2.77 (1 H, dd, 4-H), 4.01 (1 H, s, 8a-H), 7.36 (3 H, m, ArH), and 7.96 (2 H, m, 2′- and 6′-H); *m/z* 215 (M^+), 186, and 77; *m** 160.9 (215 ⟶ 186).

The signals in the ^1H n.m.r. spectrum attributable to the

two C-4 protons were analysed theoretically as the AB part of an ABX system. This treatment gave the values J_{AB} −18.4, J_{AX} 7.5, and J_{BX} 1.3 Hz, ν_A δ 2.76, and ν_B δ 2.32.

The oxazine (2g) was also prepared directly from α-chloroacetophenone oxime and cyclohexene, and was identified by comparison of its ^{1}H n.m.r. spectrum and its mass spectrum with those obtained above. The yield was extremely low and this sample was not further characterised.

3-(4-*Nitrophenyl*)-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3a). α-Bromo-4-nitroacetophenone oxime (0.581 g, 2 mmol) and styrene (2.08 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)] the *oxazine* (3a) (0.497 g, 88%), m.p. 188—189 °C (from ethanol–hexane) (Found: C, 67.55; H, 5.0; N, 10.0. $C_{16}H_{14}N_2O_3$ requires C, 68.05; H, 5.0; N, 9.9%); $\nu_{max.}$ 1 592, 1 570, and 1 505s cm^{-1}; δ 2.12—2.45 (2 H, m, 5-H$_2$), 2.72—2.82 (2 H, m, 4-H$_2$), 4.90 (1 H, dd, *J* 10.1 and 2.9 Hz, 6-H), 7.41 (5 H, s, Ph), 7.91 (2 H, d, 2′- and 6′-H), and 8.25 (2 H, d, 3′- and 5′-H); *m*/*z* 282 (*M*$^+$), 265, 253, and 77 (100%); *m** 227.0 (282 ⟶ 253).

A minor product (0.029 g; R_F 0.4) was also isolated and was identified by its ^{1}H n.m.r. spectrum as 1-(4-nitrophenyl)-4-phenylbut-3-en-1-one oxime (4a), the characteristic resonances being δ 3.76 (2 H, d, 2-H$_2$), 6.25 (1 H, m, 3-H), and 6.51 (1 H, d, 4-H). This compound was not further characterised.

6-*Methyl*-3-(4-*nitrophenyl*)-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3b). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and α-methylstyrene (2.24 g, 19 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (3b) (0.49 g, 83%), m.p. 168—172 °C (from ethanol–hexane) (Found: C, 68.6; H, 5.45; N, 9.65. $C_{17}H_{16}N_2O_3$ requires C, 68.9; H, 5.45; N, 9.45%); $\nu_{max.}$ 1 590, 1 570, and 1 500s cm^{-1}; δ 1.65 (3 H, s, 6-Me), 2.16 and 2 57 (total 4 H, 2 × m, 4-H$_2$ and 5-H$_2$), 7.37 (5 H, m, Ph), 7.78 (2 H, d, 2′- and 6′-H), and 8.17 (2 H, d, 3′- and 5′-H); *m*/*z* 296 (*M*$^+$), 279, 267, and 77; *m** 240.8 (296 ⟶ 267).

A minor product (R_F 0.3) was also isolated and was identified by its ^{1}H n.m.r. spectrum as a 1 : 1 mixture of (*Z*)- and (*E*)-1-(4-nitrophenyl)-4-phenylpent-3-en-1-one oxime (4b), the characteristic resonances being, for the *Z*-isomer, δ 2.18 (3 H, s, Me), 3.80 (2 H, d, 2-H$_2$), and 5.73 (1 H, t, 3-H), and for the *E*-isomer, δ 2.03 (3 H, s, Me), 3.67 (2 H, d, 2-H$_2$), and 5.52 (1 H, t, 3-H). These compounds were not further characterised.

3-(4-*Nitrophenyl*)-6,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3c) *and its open-chain isomer* (4c). α-Bromo-4-nitroacetophenone oxime (0.428 g, 1.65 mmol) and 1,1-diphenylethylene (1.8 g, 10 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], two products. The first to be eluted (R_F 0.8) was the *oxazine* (3c) (0.331 g, 56%), m.p. 175—176 °C (from ethanol) (Found: C, 73.55; H, 5.25; N, 8.0. $C_{22}H_{18}N_2O_3$ requires C, 73.75; H, 5.05; N, 7.8%); $\nu_{max.}$ 1 603, 1 591, and 1 506 cm^{-1}; δ 2.50 (2 H, t, 5-H$_2$), 2.79 (2 H, t, 4-H$_2$), 7.23—7.41 (6 H, m, ArH), 7.42—7.53 (4 H, m, ArH), 7.80 (2 H, d, 2′- and 6′-H), and 8.17 (2 H, d, 3′- and 5′-H); *m*/*z* 358 (*M*$^+$), 341, 329, and 105 (100%); *m** 302.4 (358 ⟶ 329) and 275.4 (358 ⟶ 314); further elution then gave 1-(4-*nitrophenyl*)-4,4-*diphenylbut*-3-*en*-1-*one oxime* (4c) (0.62 g, 10.5%) (R_F 0.4), m.p. 133—134 °C (from dichloromethane–hexane) (Found: C, 74.0; H, 4.95; N, 7.85. $C_{22}H_{18}N_2O_3$ requires C, 73.75; H, 5.05; N, 7.8%); $\nu_{max.}$ 3 250br, 1 595, 1 511, and 1 339 cm^{-1}; δ 3.71 (2 H, d, *J* 8.3 Hz, 2-H$_2$), 6.11 (1 H, t, *J* 8.3 Hz, 3-H), 7.12—7.28 (6 H, m, ArH), 7.38—7.50 (4 H, m, ArH), 7.57 (2 H, d, 2′- and 6′-H), 8.13 (2 H, d, 3′- and 5′-H), and 8.40 (1 H, br s, OH); *m*/*z* 358 (*M*$^+$), 312, 310, and 77 (100%).

In a control experiment the oxazine (3c) was stirred under normal reaction conditions (*viz.* dissolved in dichloromethane with sodium carbonate) for 24 h at room temperature. The oxazine was recovered unchanged.

The reaction of α-bromo-4-nitroacetophenone oxime and 1,1-diphenylethylene was repeated using various solvents, and the ratio of oxazine (3c) to oxime (4c) was estimated by isolation of the individual compounds. The results are given in Table 4. An attempt was also made to measure the product ratio directly from the ^{1}H n.m.r. spectrum of the crude product mixture without actual isolation of the two adducts. In these experiments α-bromo-4-nitroacetophenone oxime (0.26 g, 1 mmol), 1,1-diphenylethylene (0.2 g, 1 mmol) and sodium carbonate (1 g) were used in the solvent indicated. The approximate ratios calculated are given in Table 5. When nitromethane was employed as the solvent a further product was isolated (R_F 0.2) which was shown to be a 1 : 1 adduct of the α-halogeno-oxime and nitromethane, *viz.* 3-*nitro*-1-(4-*nitrophenyl*)*propan*-1-*one oxime* (0.073 g, 15%), m.p. 104—106 °C (from dichloromethane–hexane) (Found: C, 45.25; H, 3.8; N, 17.35. $C_9H_9N_3O_5$ requires C, 45.2; H, 3.8; N, 17.55%); $\nu_{max.}$ 3 280br, 1 600, 1 531, and 1 515 cm^{-1}; δ 3.22 (2 H, t, 2-H$_2$), 4.71 (2 H, t, 3-H$_2$), 7.41 (1 H, s, OH), 7.65 (2 H, d, 2′- and 6′-H), and 8.31 (2 H, d, 3′- and 5′-H); *m*/*z* 239 (*M*$^+$), 192, and 83 (100%); *m** 154.2 (239 ⟶ 192).

Table 4.

Solvent	Total yield (%)	Product ratio oxazine (3c) : oxime (4c)
Benzene	78	5.0 : 1
Dichloromethane	66.5	5.3 : 1
Acetonitrile	14	
Nitromethane	22	4.1 : 1

Table 5.

Solvent	Product ratio oxazine (3c) : oxime (4c)
Benzene	3.4 : 1
Dichloromethane	4.9 : 1

trans-5-*Methyl*-3-(4-*nitrophenyl*)-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3d) *and its regioisomer* (3e). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and (*E*)-1-phenylpropene (2.24 g, 19 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of regioisomers, trans-5-*methyl*-3-(4-*nitrophenyl*)-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3d) and trans-6-*methyl*-3-(4-*nitrophenyl*)-5-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3e) (0.553 g, 90%). An isomer ratio (3d) : (3e) of 56 : 44 was estimated on comparison of the relevant signals in the ^{1}H n.m.r. spectrum of the mixture, δ 0.93 [3 H, d, 5-Me of (3d)] and 1.22 [3 H, d, 6-Me of (3e)]; δ 4.04 [1 H, m, 6-H of (3e)] and 4.44 [1 H, d, 6-H of (3d)]. Recrystallisation gave a 1 : 1 mixture of the two *oxazines* (3d) and (3e), m.p. 169—185 °C (from ethanol–hexane) (Found: C, 68.6; H, 5.6; N, 9.45. $C_{17}H_{16}N_2O_3$ requires C, 68.9; H, 5.45; N, 9.45%); $\nu_{max.}$ 1 590, 1 570, 1 510s, and 1 338s cm^{-1}; δ 0.93 [1.5 H, d, *J* 5.6 Hz, 5-Me of (3d)], 1.22 [1.5 H, d, *J* 5.6 Hz, 6-Me of (3e)], 2.25—2.45 and 2.73—3.02 (total 3 H, 2 × m, 4-H$_2$ and 5-H), 4.04 [0.5 H, m, 6-H of (3e)], 4.44 [0.5 H, d, *J* 9 5 Hz, 6-H of (3d)], 7 20—7.42 (5 H, m, ArH), 7.86—7.93 (2 H, two overlapping d), and 8.20—8.27 (2 H, two overlapping d); *m*/*z* 296 (*M*$^+$), 279, and 105 (100%).

cis-5-*Methyl*-3-(4-*nitrophenyl*)-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3f). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and (*Z*)-1-phenylpropene (2.24 g, 19 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)] the *oxazine* (3f) (0.015 g, 2.5%), m.p. 202—204 °C (from ethanol–hexane) (Found: C, 68.75; H, 5.65; N, 9.4. $C_{17}H_{16}N_2O_3$ requires C, 68.9; H, 5.45; N, 9.45%); $\nu_{max.}$ 1 592, 1 568, and 1 508s cm^{-1}; δ 0.89 (3 H, d, *J* 6.8 Hz, Me), 2.40—2.60 (2 H, m,

4- and 5-H), 3.03 (1 H, dd, J −18.1 and 7.2 Hz, 4-H), 5.07 (1 H, d, J 2.0 Hz, 6-H), 7.38 (5 H, s, Ph), 7.92 (2 H, d, 2′- and 6-H), and 8.27 (2 H, d, 3′- and 5′-H); m/z 296 (M^+) and 279.

trans-6-(4-*Methoxyphenyl*)-5-*methyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3g) *and its regioisomer* (3h). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and (*Z*)-1-(4-methoxyphenyl)propene (1.48 g, 10 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of two regioisomers, trans-6-(4-*methoxyphenyl*)-5-*methyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3g) and trans-5-(4-*methoxyphenyl*)-6-*methyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3h) (0.523 g, 80%). An isomer ratio (3g) : (3h) of 87.5 : 12.5 was estimated on comparison of the relevant signals in the ^{1}H n.m.r. spectrum of the mixture, δ 0.90 [3 H, d, 5-Me of (3g)] and 1.22 [3 H, d, 6-Me of (3h)]. On attempted recrystallisation the major component preferentially crystallised to give the *oxazine* (3g), m.p. 198—199 °C (from ethanol) (Found: C, 66.5; H, 5.6; N, 8.7. $C_{18}H_{18}N_2O_4$ requires C, 66.25; H, 5.55; N, 8.6%); $\nu_{max.}$ 1 608, 1 592, 1 580, and 1 509 cm^{-1}; δ 0.90 (3 H, d, 5-Me), 2.22—2.42 (2 H, m, 4- and 5-H), 2.78—2.93 (1 H, m, 4-H), 3.81 (3 H, s, MeO), 4.38 (1 H, d, J 9.5 Hz, 6-H), 6.93 and 7.30 (total 4 H, ABq, C_6H_4OMe), and 7.91 and 8.24 (total 4 H, ABq, $C_6H_4NO_2$); m/z 326 (M^+), 309, and 135 (100%).

cis-6-(4-*Methoxyphenyl*)-5-*methyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3i) *and its* trans-*isomer* (3g). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and (*Z*)-1-(4-methoxyphenyl)propene (1.48 g, 10 mmol) containing 1% of the *E*-isomer gave, on work-up by p.l.c. (chloroform), a mixture of the *oxazine* (3i) and its *trans*-isomer (3g) in the ratio 69 : 31. The mixture was separated (p.l.c.; chloroform, 4 developments) to give the *trans*-oxazine (3g) (0.053 g, 8%), shown to be identical with an authentic sample, and the *cis*-*oxazine* (3i) (0.117 g, 18%), m.p. 199—200 °C (from dichloromethane–hexane) (Found: C, 66.45; H, 5.65; N, 8.65. $C_{18}H_{18}N_2O_4$ requires C, 66.25; H, 5.55; N, 8.6%); $\nu_{max.}$ 1 611, 1 595, 1 571, and 1 510 cm^{-1}; δ 0.91 (3 H, d, J 9.8 Hz, 5-Me), 2.49 (2 H, m, 4- and 5-H), 3.03 (1 H, dd, J −19.1 and 7.8 Hz, 4-H), 3.82 (3 H, s, MeO), 5.03 (1 H, d, J <2.0 Hz, 6-H), 6.93 and 7.32 (total 4 H, ABq, C_6H_4OMe), and 7.92 and 8.26 (total 4 H, ABq, $C_6H_4NO_2$); m/z 326 (M^+), 309, and 135 (100%).

trans-3-(4-*Nitrophenyl*)-5,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (3j). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and (*E*)-stilbene (2.4 g, 13.3 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (9 : 1)], the *oxazine* (3j) (0.409 g, 57%), m.p. 179—183 °C (from ethanol–hexane) (Found: C, 73.3; H, 5.25; N, 7.7. $C_{22}H_{18}N_2O_3$ requires C, 73.75; H, 5.05; N, 7.8%); $\nu_{max.}$ 1 590, 1 570, and 1 508s cm^{-1}; δ 2.88—3.14 (2 H, dq, 4-H_2), 3.33—3.46 (1 H, dt, 5-H), 4.88 (1 H, d, J 9.7 Hz, 6-H), 7.05—7.32 (10 H, m, 2 × Ph), 7.93 (2 H, d, 2′- and 6′-H), and 8.23 (2 H, d, 3′- and 5′-H); m/z 359, 358 (M^+), and 104 (100%).

The signals in the ^{1}H n.m.r. spectrum attributable to the two C-4 and the C-5 protons were analysed theoretically as an ABX system. This treatment gave the values J_{AB} −18.5, J_{AX} 5.7, and J_{BX} 11.5 Hz, ν_A δ 3.05, and ν_B δ 2.96.

6-*Hexyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3k) *and its regioisomer* (3l). α-Bromo-4-nitroacetophenone oxime (0.518 g, 2 mmol) and oct-1-ene (2.24 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of two regioisomers, 6-*hexyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3k) and 5-*hexyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3l) (0.232 g, 40%). An isomer ratio (3k) : (3l) of 85 : 15 was estimated on comparison of the relevant signals in the ^{1}H n.m.r. spectrum of the mixture, δ 3.73—3.88 [1 H, m, 6-H of (3k)] and 4.00—4.15 [2 H, m, 6-H_2 of (3l)]. With multiple development p.l.c. [hexane–diethyl ether (1 : 1), 4 developments] a sample of the major component was isolated as the *oxazine* (3k), m.p. 89—90 °C (from ethanol–hexane) (Found: C, 65.85; H, 7.8; N, 9.7. $C_{16}H_{22}N_2O_3$ requires C, 66.2; H, 7.65; N, 9.65%); $\nu_{max.}$ 1 592, 1 569, and 1 508s cm^{-1}; δ 0.87 (3 H, t, Me), 1.20—2.20 (12 H, m, Me[CH_2]$_5$ and 5-H_2), 2.60—2.72 (2 H, m, 4-H_2), 3.73—3.88 (1 H, m, 6-H), 7.87 (2 H, d, 2′- and 6′-H), and 8.20 (2 H, d, 3′- and 5′-H); m/z 290 (M^+), 273, and 261.

Reactions of Halogeno-oximes with 2-*Methoxypropene*.—(a) *With* α-*chloroacetophenone oxime*.* A mixture of the oxime (0.848 g, 5 mmol), 2-methoxypropene (5 cm^3), and powdered sodium carbonate (5 g) in dichloromethane (150 cm^3) was stirred overnight. The reaction mixture was filtered through Celite and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography [silica; gradient elution with 10—50% ethyl acetate in light petroleum (b.p. 60—80 °C)] which gave (i) 6-*methoxy*-6-*methyl*-3-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (2; $R^1 = R^2 = H$, $R^3 =$ OMe, $R^4 =$ Me) (0.358 g, 35%); m.p. 52 °C (from light petroleum) (Found: C, 70.1; H, 7.25; N, 6.9. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.3; N, 6.8%); $\nu_{max.}$ 1 590 and 1 555 cm^{-1}; δ 1.42 (3 H),1.69—1.85 (1 H), 1.98—2.11 (1 H, m), 2.36—2.50 (1 H, m), 2.59—2.77 (1 H, m), 3.22 (3 H), 7.30—7.37 (3 H, m), and 7.65—7.75 (2 H, m); m/z 205 (M^+); and (ii) 2-*methoxy*-2-*methyl*-5-*phenyl*-3,4-*dihydro*-2H-*pyrrole* 1-*oxide* (5a) (0.10 g, 10%), m.p. 117—120 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 70.1; H, 7.4; N, 6.7. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.3; N, 6.8%); $\nu_{max.}$ 1 540, cm^{-1}; δ 1.67 (3 H), 2.08—2.43 (2 H, m), 2.86—3.15 (2 H, m), 3.35 (3 H), 7.39—7.48 (3 H, m), and 8.38—8.46 (2 H, m); m/z 205 (M^+). The nitrone (5a) was further characterised as its adduct (6) with dimethyl acetylenedicarboxylate. The nitrone (0.15 g) and dimethyl acetylenedicarboxylate (0.50 g) in dichloromethane (20 cm^3) gave, after 48 h at room temperature, the *diester* (6) (0.10 g, 39%), m.p. 73—75 °C (from hexane) (Found: C, 62.3; H, 6.1; N, 4.1. $C_{18}H_{21}NO_6$ requires C, 62.25; H, 6.05; N, 4.0%); $\nu_{max.}$ 1 745, 1 703, and 1 655 cm^{-1}; δ 1.49 (3 H), 1.70—1.90 (1 H, m), 2.00—2.15 (1 H, m), 2.45—2.63 (1 H, m), 2.78—2.93 (1 H, m), 3.18 (3 H), 3.60 (3 H), 3.85 (3 H), 7.20—7.35 (3 H, m), and 7.50—7.60 (2 H, m).

Repetition of the cycloaddition with the chloro-oxime (2.40 g) gave the oxazine (2h) (54%) and the nitrone (5a) (8%). With acetonitrile as solvent the isolated yields were (2h) 47% and (5a) 11%.

(b) *With* α-*bromo*-4-*nitroacetophenone oxime*. A mixture of the oxime (2.05 g, 3.1 mmol), 2-methoxypropene (10 cm^3), and sodium carbonate (10 g) in dichloromethane (300 cm^3) was stirred overnight at room temperature. Column chromatography (silica) then gave (i) 6-*methoxy*-6-*methyl*-3-(4-*nitrophenyl*)-5,6-*dihydro*-4H-1,2-*oxazine* (3m) (1.61 g, 81%), m.p. 129—130 °C (from dichloromethane–light petroleum) (Found: C, 57.75; H, 5.8; N, 11.0. $C_{12}H_{14}N_2O_4$ requires C, 57.6; H, 5.6; N, 11.2%); $\nu_{max.}$ 1 593, 1 574, and 1 505 cm^{-1}; δ 1.49 (3 H), 1.75—1.92 (1 H, m), 2.08—2.20 (1 H, m), 2.41—2.55 (1 H, m), 2.66—2.85 (1 H, m), 3.24 (3 H), 7.84—7.92 (2 H, m), and 8.18—8.26 (2 H, m); m/z 250 (M^+); and (ii) 2-*methoxy*-2-*methyl*-5-(4-*nitrophenyl*)-3,4-*dihydro*-2H-*pyrrole* 1-*oxide* (5b) (0.210 g, 11%), m.p. 150—152 °C (from ethyl acetate–light petroleum) (Found: C, 57.9; H, 5.8; N, 11.1. $C_{12}H_{14}N_2O_2$ requires C, 57.6; H, 5.6; N, 11.2%); $\nu_{max.}$ 1 587, 1 538, and 1 495 cm^{-1}; δ 1.61 (3 H), 2.14—2.47 (2 H, m), 2.93—3.23 (2 H, m), 3.34 (3 H), 8.20—8.28 (2 H, m), and 8.55—8.63 (2 H, m); m/z 250 (M^+).

(c) *With* syn- *and* anti-α-*bromoacetophenone oximes*. The *anti*-oxime was prepared from the *syn*-oxime as described in the literature.[8] Each oxime (0.420 g) was dissolved in a

* Preliminary experiments were carried out by Dr. G. M. Iskander.

mixture of 2-methoxypropene (1.50 g) and dichloromethane (120 cm^3) containing sodium carbonate (5.0 g). The two reaction mixtures were stirred for 24 h and then filtered. The filtrates were evaporated and the residues were analysed by ^1H n.m.r. spectroscopy. Both showed signals due to the oxazine (2h) and the nitrone (5a) in identical ratios of 8 : 1.

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