Addition and Cycloaddition Reactions of the Electrophilic Vinyl Nitroso Compounds 3-Nitrosobut-3-en-2-one, 2-Nitrosopropenal, and Ethyl 2-Nitrosopropenoate [1]

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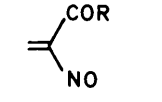
1-Chlorobutane-2,3-dione 2-oxime (2a) reacts with sodium carbonate and, in the presence of olefins, gives the oxazines (4) stereoselectively and in good yield. 3-Nitrosobut-3-en-2-one (1a) is postulated to be the intermediate in these reactions. Similar additions occur with 3-chloro-2-hydroxyiminopropanal (2b) and with ethyl bromopyruvate 2-oxime (3), although the oxazines are generally formed in lower yield. Competition experiments using pairs of olefins indicate that the intermediate (1a) adds preferentially to electron-rich olefins.

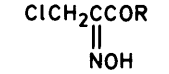
The vinyl nitroso intermediates (1) act as electrophiles towards indole; the products are the corresponding 3-alkylindoles (11). Analogous reactions are observed with pyrrole, 1-methylpyrrole, 1,3-dimethoxybenzene, and *NN*-dimethylaniline; with 3-methylindole, addition takes place at the 3-position to give the cycloadducts (12).

3-Nitrosopent-3-en-2-one (19) has been generated from 4-chloropentane-2,3-dione 3-oxime. This vinyl nitroso intermediate also undergoes cycloaddition to olefins, in competition with a hydrogen shift from the terminal methyl group which leads to isomerisation to pent-2-ene-2,3-dione 3-oxime (20).

In the preceding paper [2] it was shown that α-nitrosostyrenes act as electron-deficient heterodienes in cycloaddition reactions. We considered that the cycloadditions could provide a useful general route to 5,6-dihydro-4*H*-1,2-oxazines (a) if the electrophilic character, and hence the reactivity, of the vinyl nitroso intermediates could be further increased, and (b) if the aryl substituents could be replaced by functional groups more suitable for further transformations. In this paper we describe the generation and some reactions of three such vinyl nitroso intermediates, (1a—c). The introduction of acyl and ethoxycarbonyl groups in this position should greatly increase the electrophilic character of the terminal carbon atom, and these groups should be suitable for a wide range of further reactions in the dihydro-1,2-oxazine cycloadducts.



(1) a; R = Me
b; R = H
c; R = OEt



(2) a; R = Me
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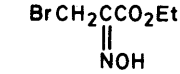

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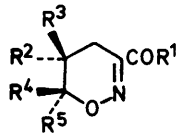


(4) R^1 = Me
(5) R^1 = H
(6) R^1 = OEt

Preparation of Halogeno-oximes.—The vinyl nitroso compounds (1a) and (1b) were generated from the chloro-oximes (2). These chloro-oximes have been reported previously. The acetyl oxime (2a) has been prepared from 4-chlorobutan-2-one and ethyl nitrite,[3] and from the addition of nitrosyl chloride to but-3-en-2-one.[4] The latter method provides a very efficient route to the chloro-oxime but requires nitrosyl chloride gas. We found that the chloro-oxime could also be prepared from but-3-en-2-one, ethyl nitrite, and hydrochloric acid in ethanol. The product is a crystalline solid which can be stored at 0 °C for several months without decomposition. The chloro-oxime (2b) was prepared as a viscous oil by the addition of nitrosyl chloride to acrylaldehyde.[5] The addition of nitrosyl chloride to acrylic esters is not a satisfactory route to chloro-oximes;[6] instead, the bromo-oxime (3) was prepared, as a precursor of the nitrosoacrylate ester (1c), by the reaction of ethyl bromopyruvate with hydroxylamine sulphate. This bromo-oxime is a crystalline solid which can be stored without decomposition for several months.

Formation of Dihydro-oxazines.—The vinyl nitroso intermediates (1) were generated from the halogeno-oximes by stirring the latter with anhydrous sodium carbonate in dichloromethane at room temperature for 24 h. No blue colour was detected in the solutions and the evidence for the intermediacy of the vinyl nitroso compounds is indirect, being based on trapping experiments.

The chloro-oxime (2a) gave the dihydro-oxazines (4) when the dehydrochlorination was carried out in the presence of a wide range of olefins. These included not only conjugated dienes and styrenes, but also simple alkenes such as cyclohexene, oct-1-ene, and cyclo-octene. The oxazines (4) were isolated in moderate-to-good yield when a five-fold excess of the olefin was used. As might be expected for a cycloaddition involving 'inverse electron demand,' more electron-deficient olefins failed to react: no cycloadducts were obtained from (*E*)-1,2-dichloroethylene, or from diethyl fumarate. The 3-acetyloxazines (4) which were isolated from these reactions are listed in Table 1.

These cycloadditions are similar to those observed with 4-nitro-α-nitrosostyrene,[2] although additions to (*E*)-1-phenylpropene, (*E*)-1-(4-methoxyphenyl)propene, and oct-1-ene are much more regioselective. Additions to (*E*)- and (*Z*)-cyclooctene are completely stereoselective, which indicates that the additions are unlikely to involve zwitterionic intermediates. The reactions with (*Z*)-1-phenylpropene and (*Z*)-1-(4-methoxyphenyl)propene gave low yields of adducts in which a minor component had the *E*-stereochemistry. These may well

Table 1. 3-Acetyl-5,6-dihydro-4*H*-1,2-oxazines (4)

Substrate	Oxazine	R^2	R^3	R^4	R^5	Yield (%) [a]
α-Methylstyrene	(4a)	H	H	Me	Ph	43
(*E*)-1-Phenylpropene	(4b)	H	Me	H	Ph	36 [b]
	(4c)	H	Ph	H	Me	
(*Z*)-1-Phenylpropene	(4d)	H	Me	Ph	H	14 [c]
(*E*)-1-(4-Methoxyphenyl)propene	(4e)	H	Me	H	C_6H_4OMe-4	53
(*Z*)-1-(4-Methoxyphenyl)propene	(4f)	H	Me	C_6H_4OMe-4	H	30 [d]
(*E*)-Stilbene	(4g)	H	Ph	H	Ph	46
Oct-1-ene	(4h)	H	H	H	C_6H_{13}	31
Cyclohexene	(4i)	H	$-[CH_2]_4-$		H	21
(*Z*)-Cyclo-octene	(4j)	H	$-[CH_2]_6-$		H	60
(*E*)-Cyclo-octene	(4k)	H	*e*	H	*e*	81
Norbornene	(4l)	H	$-CH[CH_2]_2CH-$		H	60 [f]
Ethyl vinyl ether	(4m)	H	H	H	OEt	82
Furan	(4n)	H	$-OCH=CH-$		H	75
2,5-Dimethylfuran	(4o)	Me	$-OC(Me)=CH-$		H	58
Benzofuran	(4p)	H	$-OC_6H_4-$		H	35

[a] Isolated yields, except where indicated, reproducible within 3%. [b] Ratio (by n.m.r.) (4b) : (4c) 87 : 13. Isomer (4b) only isolated. [c] Contains 19% isomer (4b); see text. [d] Contains 29% isomer (4e); see text. [e] $R^3R^5 = [CH_2]_6$. [f] *exo*-Isomer.

Table 2. 3-Formyl-5,6-dihydro-4*H*-1,2-oxazines (5)

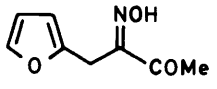
Substrate	Oxazine	R^2	R^3	R^4	R^5	Yield (%)
α-Methylstyrene	(5a)	H	H	Me	Ph	39
(*E*)-Stilbene	(5b)	H	Ph	H	Ph	13
Oct-1-ene	(5c)	H	H	H	C_6H_{13}	18
(*Z*)-Cyclo-octene	(5d)	H	$-[CH_2]_6-$		H	41
Cyclopentadiene	(5e)	H	$-CH_2CH=CH-$		H	76

have been formed by addition to traces of the much more reactive *E*-isomers in the starting olefins, however. This was indicated by a series of experiments in which the (*Z*)-1-(4-methoxyphenyl)propene, recovered after reaction with the chloro-oxime, was used as a substrate for further addition. After two such experiments the yield of cycloadduct had fallen from 30 to 20%, but the proportion of *E*-isomer (4e) in the product mixture had fallen from 29 to 6%. All the other cycloadditions shown in Table 1 were completely regio- and stereo-selective, within the limits of detection by ^1H n.m.r.

The relative reactivities of four of the substrates shown in Table 1 were compared by allowing them to compete in pairs for a deficiency of the nitrosovinyl ketone (1a). With equimolar amounts of the pairs of substrates each present in a five-fold excess, the following results were obtained: (i) α-methylstyrene and norbornene gave only the α-methylstyrene adduct (4a). (ii) α-Methylstyrene and 2,5-dimethylfuran gave only the 2,5-dimethylfuran adduct (4o). (iii) 2,5-Dimethylfuran and ethyl vinyl ether gave a 1 : 1 mixture of the adducts (4o) and (4m). The relative order of reactivity, norbornene $\ll$ α-methylstyrene $\ll$ 2,5-dimethylfuran $\sim$ ethyl vinyl ether, is as expected for the cycloaddition of an electrophilic diene.

The furan adduct (4n) isomerised to the oxime (7) within a few hours at room temperature. A similar isomerisation of the benzofuran adduct (4p) to the oxime (8) took place when it was treated with acid; [7] the ^1H n.m.r. spectrum of compound (8) (δ 6.34 for 3-H) helped to confirm the direction of the cycloaddition to benzofuran.

Reactions of the chloro-oxime (2b) and a limited range of olefinic substrates were carried out in a similar manner to those with compound (2a). The 3-formyl-1,2-oxazines (5) which were characterised are shown in Table 2. The reactions



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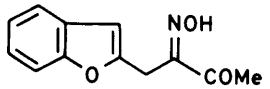


(8)

appeared to be less clean than those of the chloro-oxime (2a) and the yields of cycloadducts were generally lower.

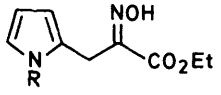
Analogous reactions with ethyl bromopyruvate 2-oxime (3) showed that the nitrosoacrylate ester (1c) is significantly less reactive in cycloadditions than the nitroso ketone (1a). Simple alkenes gave adducts (6) only in very poor yield, and the reaction was successful only with conjugated olefins and dienes.* The oxazines (6) which were characterised are shown in Table 3. No adducts were detected with cyclohexene or with benzofuran.

N.M.R. Spectra.—The ^1H n.m.r. spectra of the oxazines were used as the basis for deducing the stereoselectivities of the additions. For the oxazines bearing a single substituent at the 6-position [such as the octene adduct (4h)] or for those bearing substituents at C-5 and C-6 in a *trans* arrangement, the spectra can be interpreted by assuming a half-chair conformation for the oxazines with the substituents in equatorial positions. In such compounds $J_{5,6}$ is large (usually *ca.* 10 Hz), indicating a *trans* diaxial arrangement of the coupled hydrogen atoms. The only exception to this is the vinyl ether adduct (4m) in which both 5-H-to-6-H couplings are small, indicating that the ethoxy group is axial. This conformation is also the preferred

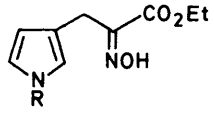
* Enol ethers also give oxazines in satisfactory yield (W. Stretch, unpublished work).

Table 3. 3-Ethoxycarbonyl-5,6-dihydro-4*H*-1,2-oxazines (6)

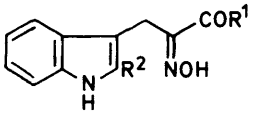
Substrate	Oxazine	R^2	R^3	R^4	R^5	Yield (%)
Styrene	(6a)	H	H	H	Ph	5
α-Methylstyrene	(6b)	H	H	Me	Ph	43
1,1-Diphenylethylene	(6c)	H	H	Ph	Ph	7
Oct-1-ene	(6d)	H	H	H	C_6H_{13}	2.5
Indene	(6e)	H	$-CH_2C_6H_4-$		H	53
Cyclopentadiene	(6f)	H	$-CH_2CH=CH-$		H	79
6,6-Dimethylfulvene	(6g)	H	$Me_2C=CCH=CH-$		H	37
Furan	(6h)	H	$-OCH=CH-$		H	46



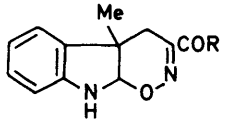
(9) a; R = H
b; R = Me



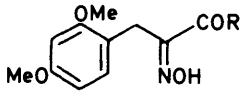
(10) a; R = H
b; R = Me



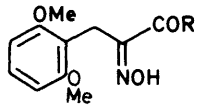
(11) a; R^1 = Me, R^2 = H (73%)
b; R^1 = OEt, R^2 = H (82%)
c; R^1 = R^2 = Me (65%)



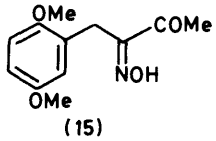
(12) a; R = Me (86%)
b; R = OEt (81%)



(13) a; R = Me
b; R = H
c; R = OEt



(14) a; R = Me
b; R = H
c; R = OEt



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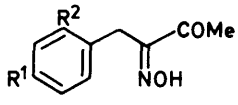
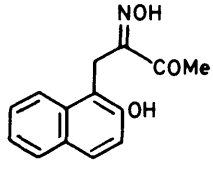


(16) R^1 = H, R^2 = NMe_2
(17) R^1 = NMe_2, R^2 = H



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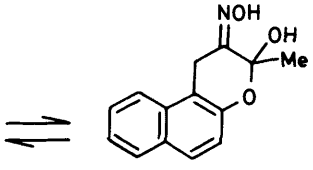


(18b)

one for the analogous pyran, 2-ethoxy-3,4-dihydro-2*H*-pyran, and the preference has been ascribed to the anomeric effect.[8]

For *cis*-5,6-disubstituted oxazines, 6-H is found at *ca.* 0.5—0.7 p.p.m. downfield from its position in the corresponding *trans*-isomer, and $J_{5,6}$ is small (*ca.* 2 Hz). These features are consistent with an axial position for the 6-substituent and an equatorial position for the 5-substituent. There is also a reduction in the coupling constant between the *trans*-disposed hydrogens 4-H and 5-H [for example, $J_{4,4a}$ is 7.1 Hz in the (*Z*)-cyclo-octene adduct (4j), but it is 12.7 Hz in the *E*-adduct (4k)], which may be due to distortion of the ring by the axial substituent at C-6 (C-10a in systematic numbering).

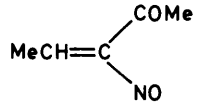
Additions to Pyrroles, Indoles, and Other Aromatic Systems.—We have investigated the uses of these vinyl nitroso compounds as alkylating agents for nucleophilic aromatic systems with a small range of substrates. The reagents are attractive as alkylating agents because of the mild, non-acidic conditions in which they are generated and because of the variety of potential functional groups which can be introduced. For example, we considered that the nitroso ester (1c) was potentially a good synthon for producing esters of α-amino acids.[1c] Thus, most of the reactions were carried out with ethyl bromopyruvate 2-oxime (3), although where direct comparisons were made, the intermediates generated from the acyl chloro-oximes (2) proved to be better alkylating agents.

Pyrrole reacted with the bromo-oxime (3) in the presence of sodium carbonate to give a mixture of the 2- and 3-substitution products (9a) and (10a) (86 : 14) which was isolated in 55% yield. *N*-Methylpyrrole gave an 80 : 20 mixture of the corresponding pyrroles (9b) and (10b) (53%). Indole gave exclusively the 3-substitution products (11a, b) with the acetyl- and ethoxycarbonyl-nitroso intermediates. These reactions were initially performed with an excess of indole, but the adduct (11b) was also isolated in good yield from one equivalent of indole. With 2-methylindole, the chloro-oxime (2a) gave the 3-substitution product (11c).

3-Methylindole proved to be an excellent substrate and gave the cycloadducts (12) resulting from exclusive attack at the 3-position. The reaction thus appears to have potential as a method of alkylation of 3-substituted indoles. It is not possible to deduce from these preliminary experiments whether the adducts are formed by a cycloaddition process, or whether it is a 3-alkylation followed by ring closure at the 2-position. However, the isolation of cycloadducts from the less aromatic furan and benzofuran, and their ready isomerisation to the oximes (7) and (8), indicate that all these adducts might be formed by initial cycloaddition, followed by a proton transfer where this is possible.

Attempts to extend the alkylations to simple benzenoid aromatics were largely unsuccessful. Anisole failed to react with the chloro-oxime (2a), but 1,3-dimethoxybenzene gave a *ca.* 4 : 1 mixture of the 4- and 2-substitution products (13a) and (14a) in 63% yield. The halogeno-oximes (2b) and (3) reacted in a similar manner and gave *ca.* 4 : 1 mixtures of alkylation products in yields of 41 and 11%, respectively. 1,4-Dimethoxybenzene gave the adduct (15) in low yield from the chloro-oxime (2a), but 1,2-dimethoxybenzene failed to give an alkylation product.

The vinyl nitroso compound (1a) also gave alkylation products with *NN*-dimethylaniline and with 2-naphthol in low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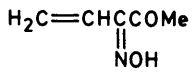
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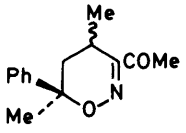
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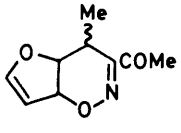
(22)

yield. These had the expected structures (16) and (17), and (18), the β-naphthol adduct (18) existing as a mixture of ring- and open-tautomer in solution. The nitroso-ester (1c) failed to give an adduct with β-naphthol.

3-*Nitrosopent*-3-*en*-2-*one*.—The nitroso intermediate (19) was generated and its chemistry was investigated briefly, in order to determine whether a β-alkyl substituent would inhibit the cycloaddition reactions. Unlike the vinyl nitroso compounds (1), this and similar compounds have a potentially easy mode of intramolecular rearrangement available; namely, the isomerisation to an unsaturated oxime, in this case compound (20). Similar rearrangements have been observed, and have been represented as [1,5] sigmatropic hydrogen shifts,[9] but it is by no means established that the alkyl and nitroso groups need to be *cis* for the rearrangement to occur.

The vinyl nitroso compound (19) was generated from 4-chloropentane-2,3-dione 3-oxime [10] in the usual way, in the presence of either α-methylstyrene or furan. The cycloadducts (21) and (22) were isolated as mixtures of diastereoisomers, together with the unsaturated oxime (20). Thus, the hydrogen shift does not completely suppress the cycloaddition reactions and the latter do not seem to be inhibited by steric or electronic effects of the β-methyl group.

Conclusions.—We have shown that vinyl nitroso compounds bearing additional activating substituents (COMe, CHO, CO_2Et), at the α-carbon atom can be generated from halogeno-oximes and can be intercepted by olefins. The cycloadditions are, in general, both regio- and stereo-selective. The acetyl-substituted intermediate (1a) gives oxazines in the best yields. The vinyl nitroso compounds are also useful alkylating agents for electron-rich heterocycles. The adducts and cycloadducts formed in this way bear an interesting array of functional groups which makes them potentially useful starting materials for further transformations.

Experimental

General points, and methods used for the preparation of (*Z*)-1-arylpropenes, are described in the preceding paper.[2]

1-*Chlorobutane*-2,3-*dione* 2-*Oxime* (2a).[4]—Nitrosyl chloride (31 g, 0.47 mol) was condensed into a cold trap (acetone–solid CO_2) and was then added slowly during 1 h to a stirred solution of but-3-en-2-one (34.2 g, 0.49 mol) in dry diethyl ether (150 cm^3) cooled to −20 °C (tetrachloromethane–solid CO_2 bath). After 2 h the solvent was removed under reduced pressure to leave a pale-green solid which was washed with cold tetrachloromethane (100 cm^3) and then recrystallised from hot (*not* boiling) tetrachloromethane to give 1-chlorobutane-2,3-dione 2-oxime (2a) (57.6 g, 87%), m.p. 88—89 °C (from CCl_4) (lit.,[4] 86%, m.p. 89—90 °C); δ 2.45 (3 H, Me), 4.39 (2 H, CH_2Cl), and 9.29 (1 H, OH).

The oxime was also prepared using ethyl nitrite as follows. But-3-en-2-one (14 g), ethanol (5 cm^3) and ethyl nitrite (21 g) were stirred at −40 °C in a two-necked flask fitted with a CO_2 condenser. Concentrated hydrochloric acid (40 cm^3) was added dropwise during 20 min. A yellow precipitate appeared. The mixture was then stirred at −40 °C for 30 min and filtered while cold. The precipitate was washed with water, dried, and crystallised to give the oxime (2a) (16.8 g, 62%).

4-*Chloropentane*-2,3-*dione* 3-*Oxime*.[10]—Nitrosyl chloride (14 g, 0.214 mol) was added to a solution of pent-3-en-2-one (19 g, 0.225 mol) in dry diethyl ether (10 cm^3) at −20 °C; work-up as above gave 4-chloropentane-2,3-dione 3-oxime (14.3 g, 45%), m.p. 81—82 °C (from benzene–hexane) (lit.,[10] 51%, m.p. 82 °C); δ 1.81 (3 H, d, Me), 2.41 (3 H, MeCO), 5.42 (1 H, q, 4-H), and 9.12 (1 H, OH).

3-*Chloro*-2-*hydroxyiminopropanal* (2b).[5]—Nitrosyl chloride (65.5 g, 1 mol) was added slowly during 4 h to a solution of acrylaldehyde (56 g, 1 mol) in dry diethyl ether (400 cm^3) at −20 °C; work-up as above gave 3-chloro-2-hydroxyiminopropanal (2b) (120 g, 99%) as a pale-yellow, viscous oil which solidified when kept at below −20 °C; δ 4.29 (2 H, CH_2Cl), 9.51 (1 H, CHO), and 10.21 (1 H, br, OH).

Ethyl Bromopyruvate 2-*Oxime* (3).—A solution of hydroxylamine sulphate (10 g, 60 mmol) in water (60 cm^3) was added to one of ethyl bromopyruvate (11.7 g, 60 mmol) in chloroform (20 cm^3) and the two-phase system was rapidly stirred for 22 h at 20 °C. The mixture was extracted with chloroform (3 × 75 cm^3) and the combined organic extracts were dried (Na_2SO_4). The solvent was removed under reduced pressure to give a yellow oil which solidified with time. This crude solid (9.97 g) was recrystallised to give *ethyl bromopyruvate* 2-*oxime* (3) (6.31 g, 50%), m.p. 76—79 °C (from hexane) (Found: C, 28.4; H, 3.85; N, 6.45. $C_5H_8BrNO_3$ requires C, 28.6; H, 3.85; N, 6.65%); $\nu_{max.}$ 3 450—3 000br, 1 720, and 1 028 cm^{-1}; δ 1.36 (3 H, t), 4.27 (2 H, CH_2Br), 4.39 (2 H, q), and 9.48 (1 H, br, OH); *m*/*z* 211 and 209 (1 : 1, M^+), 183 and 181 (1 : 1), and 101 (100%); *m** 156.8 (209 ⟶ 181) and 158.7 (211 ⟶ 183).

Attempts to carry out this oximation in alcoholic solvents gave, in our hands, the bromo-oxime contaminated with the product of displacement of bromide by the alcohol. Subsequently, a procedure has been reported which gives good yields of the bromo-oxime in methanolic solution.[11]

Reactions of Halogeno-oximes.—*General procedure*. The following method was used when treating the oxime with olefins, heterocycles, and other substrates. The halogeno-oxime (2 mmol) was dissolved in dry dichloromethane (50 cm^3) with an excess of the substrate (5—20 mmol). 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-*Acetyl*-6-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4a). 1-Chlorobutane-2,3-dione 2-oxime (2a) (0.271 g, 2 mmol) and α-methylstyrene (2.24 g, 19 mmol) gave, on work-up by preparative layer chromatography [p.l.c.; chloroform–ethyl acetate (19 : 1) as developer], the oxazine (4a) (0.189 g, 43%) as a yellow oil; $\nu_{max.}$ 1 697 cm^{-1}; δ 1.60 (3 H, 6-Me), 1.65—1.95 and 2.32—2.52 (total 4 H, 2 × m, 4- and 5-H_2), 2.37 (3 H, MeCO), and 7.25—7.35 (5 H, m, Ph); *m*/*z* 217 (M^+), 200, 174, 158, 143, and 77; *m** 184.3 (217 ⟶ 200), 139.5 (217 ⟶ 174

129.4 (158 ⟶ 143), and 124.8 (200 ⟶ 158). The adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 217—218 °C (from chloroform–ethanol) (Found: C, 57.1; H, 5.05; N, 17.45. $C_{19}H_{19}N_5O_5$ requires C, 57.45; H, 4.8; N, 17.6%); δ 1.64 (3 H, 6-Me), 1.92—2.16 and 2.41—2.88 (total 4 H, 2 × m, 4- and 5-H_2), 2.31 (3 H), 7.25—7.41 (5 H, m, Ph), 7.87 (1 H, d, 6′-H), 8.31 (1 H, dd, 5′-H), 9.12 (1 H, d, 3′-H), and 11.0 (1 H, NH); *m/z* 397 (M^+).

trans-3-*Acetyl*-5-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4b) *and its regioisomer* (4c). 1-Chlorobutane-2,3-dione 2-oxime (0.271 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-3-*acetyl*-5-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4b) and trans-3-*acetyl*-6-*methyl*-5-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4c) (0.158 g, 36%). An isomer ratio (4b) : (4c) of 87 : 13 was estimated on comparison of the relevant signals in the ^{1}H n.m.r. spectrum of the mixture, δ 0.83 [3 H, d, *J* 6.6 Hz, 5-Me of (4b)] and 1.15 [3 H, d, *J* 6.6 Hz, 6-Me of (4c)]. On attempted recrystallisation the major component preferentially crystallised to give the *oxazine* (4b), m.p. 55—56 °C (from hexane) (Found: C, 71.95; H, 7.0; N, 6.65. $C_{13}H_{15}NO_2$ requires C, 71.85; H, 6.95; N, 6.45%); $\nu_{max.}$ 1 685 and 1 585 cm^{-1}; δ 0.83 (3 H, d, *J* 6.6 Hz, 5-Me), 1.90—2.15 (2 H, m, 4- and 5-H), 2.44 (3 H, MeCO), 2.73 (1 H, m, 4-H), 4.34 (1 H, d, *J* 9.8 Hz, 6-H), and 7.30—7.41 (5 H, m, Ph); *m/z* 217 (M^+).

cis-3-*Acetyl*-5-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4d). 1-Chlorobutane-2,3-dione 2-oxime (0.271 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)], a mixture of cis-3-*acetyl*-5-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4d) and its *trans*-isomer (4b) in the ratio 81 : 19 (0.061 g, 14%). The presence of the two isomers was indicated by the characteristic resonance of the respective C-6 proton, δ 4.34 [1 H, d, *J* 9.8 Hz, 6-H of (4b)] and 4.97 [1 H, d, *J* 2.0 Hz, 6-H of (4d)]. The mixture was treated with 2,4-dinitrophenylhydrazine and the product was subjected to p.l.c. (chloroform, 3 developments) to give the 2,4-*dinitrophenylhydrazone* of the *cis*-oxazine (4d), m.p. 198—200 °C (from chloroform–ethanol) (Found: C, 57.4; H, 4.75; N, 17.55. $C_{19}H_{19}N_5O_5$ requires C, 57.45; H, 4.8; N, 17.6%); $\nu_{max.}$ 3 300, 1 610, and 1 590 cm^{-1}; δ 0.85 (3 H, d, *J* 6.6 Hz, 5-Me), 2.38 (3 H, Me), 2.39—2.51 (1 H, m, 5-H), 2.70 and 2.93 (total 2 H, dq, 4-H), 5.04 (1 H, d, *J* 2.0 Hz, 6-H), 7.38 (5 H, Ph), 7.99 (1 H, d, 6′-H), 8.37 (1 H, dd, 5′-H), 9.15 (1 H, d, 3′-H), and 11.2 (1 H, NH); *m/z* 397 (M^+). The signals in the ^{1}H n.m.r. spectrum attributable to the C-4 protons were analysed theoretically as the AB part of an ABX system. This treatment gave the values J_{AB} −18.5, J_{AX} 6.9, and J_{BX} 1.7 Hz, ν_A δ 2.91, and ν_B δ 2.70.

In control experiments, the isomers (4b) and (4d) were not interconverted under the reaction conditions (sodium carbonate in dichloromethene), and were not interconverted when heated at 100 °C using a polar solvent (nitromethane).

trans-3-*Acetyl*-6-(4-*methoxyphenyl*)-5-*methyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4e). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and (*E*)-1-(4-methoxyphenyl)propene (1.48 g, 10 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the oxazine (4e) (0.266 g, 53.5%) as an oil; $\nu_{max.}$ 1 692 and 1 612 cm^{-1}; δ 0.82, (3 H, d, *J* 7.3 Hz, 5-Me), 1.88—2.11 (2 H, m, 4- and 5-H), 2.43 (3 H, MeCO), 2.69—2.80 (1 H, m, 4-H), 3.81 (3 H, MeO), 4.29 (1 H, d, *J* 10.8 Hz, 6-H), and 6.92 and 7.26 (total 4 H, ABq, C_6H_4OMe); *m/z* 247 (M^+), 230, 188, 148, and 135 (100%); *m** 214.2 (247 ⟶ 230). The adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 161—162 °C (from ethanol) (Found: C, 56.5; H, 5.05; N, 16.65. $C_{20}H_{21}N_5O_6$ requires C, 56.2; H, 4.95; N, 16.4%); $\nu_{max.}$ 3 300, 1 715, 1 692, and 1 605 cm^{-1}; δ 0.91 (3 H, d, *J* 7.3 Hz, 5-Me), 2.15—2.35 (2 H, m, 4- and 5-H), 2.36 (3 H), 2.96—3.09 (1 H, m, 4-H), 3.82 (3 H, MeO), 4.37 (1 H, d, *J* 9.8 Hz, 6-H), 6.93 and 7.29 (total 4 H, ABq, C_6H_4OMe), 7.99 (1 H, d, 6′-H), 8.38 (1 H, dd, 5′-H), 9.15 (1 H, d, 3′-H), and 11.29 (1 H, NH); *m/z* 427 (M^+), 246, and 135 (100%).

Table 4.

Total yield	Product ratio (4f) : (4e)
(a) 0.151 g, 30.5%	71 : 29
(b) 0.097 g, 20%	87 : 13
(c) 0.102 g, 20.5%	93.5 : 6.5

cis-3-*Acetyl*-6-(4-*methoxyphenyl*)-5-*methyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4f). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and (*Z*)-1-(4-methoxyphenyl)propene * (1.48 g, 10 mmol) gave, on work-up by p.l.c. (chloroform), a mixture of cis-3-*acetyl*-6-(4-*methoxyphenyl*)-5-*methyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4f) and its *trans*-isomer (4e) in the ratio 71 : 29 (0.151 g, 30.5%); thus, the yields of the respective isomers were *cis* (0.107 g, 21.5%) and *trans* (0.044 g, 9%). The mixture was treated with 2,4-dinitrophenylhydrazine, and the products were separated by p.l.c. (chloroform, 7 developments) to give the 2,4-dinitrophenylhydrazone of the *trans*-oxazine (4e), shown to be identical with an authentic sample, and the 2,4-*dinitrophenylhydrazone* of the *cis*-oxazine (4f), m.p. 163—165 °C (from ethanol) (Found: C, 55.85; H, 5.25; N, 16.35. $C_{20}H_{21}N_5O_6$ requires C, 56.2; H, 4.95; N, 16.4%); $\nu_{max.}$ 3 315, 1 612, 1 590, and 1 511 cm^{-1}; δ 0.84 (3 H, d, *J* 6.9 Hz, 5-Me), 2.36 (3 H), 2.35—2.49 (1 H, m, 5-H), 2.68 (1 H, dd, *J* −18.9 and 2.9 Hz, 4-H), 2.90 (1 H, dd, *J* −18.9 and 7.2 Hz, 4-H), 3.80 (3 H, MeO), 4.97 (1 H, d, *J* 2.3 Hz, 6-H), 6.90 and 7.28 (total 4 H, ABq, C_6H_4OMe), 7.97 (1 H, d, 6′-H), 8.33 (1 H, dd, 5′-H), 9.09 (1 H, d, 3′-H), and 11.26 (1 H, NH); *m/z* 427 (M^+) and 135 (100%).

The excess of olefin from the above experiment (a) was recovered and re-used in a repeat experiment (b). In turn, the excess of olefin from this second experiment was recovered and used again in a third experiment (c). The results of these experiments are given in Table 4. The mixture from the third experiment (c) solidified on standing, and was preferentially crystallised to give cis-3-*acetyl*-6-(4-*methoxyphenyl*)-5-*methyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4f), m.p. 65—66 °C (from diethyl ether–pentane) (Found: C, 68.15; H, 6.8; N, 5.85. $C_{14}H_{17}NO_3$ requires C, 68.0; H, 6.96; N, 5.65%); $\nu_{max.}$ 1 682, 1 613, and 1 591 cm^{-1}; δ 0.76 (3 H, d, *J* 6.4 Hz, 5-Me), 2.22—2.42 (2 H, m, 4- and 5-H), 2.45 (3 H, MeCO), 2.60 (1 H, dd, *J* −20.5 and 7.3 Hz, 4-H), 3.81 (3 H, MeO), 4.92 (1 H, d, *J* 2.0 Hz, 6-H), and 6.92 and 7.27 (total 4 H, ABq, C_6H_4OMe); *m/z* 247 (M^+), 230, 188, 148, 135 (100%), and 121; *m** 214.2 (247 ⟶ 230) and 153.7 (230 ⟶ 188).

trans-3-*Acetyl*-5,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4g). 1-Chlorobutane-2,3-dione 2-oxime (0.271 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* (4g) (0.258 g, 46%), m.p. 108—111 °C (from ethanol–hexane) (Found: C, 77.4; H, 6.2; N, 5.05. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.15; N, 5.0%); $\nu_{max.}$ 1 685 cm^{-1}; δ 2.47 (3 H, MeCO), 2.59 and 2.93 (total 2 H, dq, 4-H_2), 3.11 (1 H, dt, 5-H), 4.78 (1 H, d, *J* 10.0 Hz, 6-H), and 6.92—7.24 (10 H, m, 2 × Ph); *m/z* 279 (M^+).

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 spectrum. This treatment gave the values J_{AB} −19.2, J_{AX} 5.1, and J_{BX} 11.2 Hz, ν_A δ 2.93 and ν_B δ 2.60.

* The olefin was shown by g.l.c. to contain 1% *E*-isomer; thus, the olefin used contained 0.1 mmol of the *E*-isomer.

3-*Acetyl*-6-*hexyl*-5,6-*dihydro*-4H-1,2-*oxazine* (4h). 1-Chlorobutane-2,3-dione 2-oxime (0.271 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)], the oxazine (4h) (0.134 g, 31.5%) as a yellow oil; δ 0.85—0.95 (3 H, m), 1.25—1.83 (10 H, m), 1.92—2.63 (4 H, m, 4- and 5-H), 2.40 (3 H, MeCO), and 3.75 (1 H, m, 6-H); the adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 125—126 °C (from chloroform–ethanol) (Found: C, 55.35; H, 6.6; N, 17.95. $C_{18}H_{25}N_5O_5$ requires C, 55.25; H, 6.45; N, 17.9%); $\nu_{max.}$ 3 315, 1 615, and 1 586 cm^{-1}; δ 0.88 (3 H, t), 1.25—1.88 (11 H, m), 1.98—2.17 (1 H, m, 5-H), 2.31 (3 H), 2.40—2.63 (1 H, m, 4-H), 2.77—2.92 (1 H, dd, 4-H), 3.79 (1 H, m, 6-H), 7.96 (1 H, d, 6′-H), 8.35 (1 H, dd, 5′-H), 9.12 (1 H, d, 3′-H), and 11.27 (1 H, NH); *m/z* 391 (M^+).

cis-3-*Acetyl*-4a,5,6,7,8,8a-*hexahydro*-4H-1,2-*benzoxazine* (4i). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and cyclohexene (2.5 g, 30 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the oxazine (4i) (0.078 g, 21.5%) as a yellow oil; δ 1.15—2.23 (9 H, m, 5-, 6-, 7-, and 8-H_2 and 4a-H), 2.29—2.38 (2 H, m, 4-H_2), 2.41 (3 H, MeCO), and 3.99 (1 H, m, 8a-H); the adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 146—148 °C (from chloroform–ethanol) (Found: C, 53.05; H, 5.35; N, 19.25. $C_{16}H_{19}N_5O_5$ requires C, 53.2; H, 5.3; N, 19.4%); $\nu_{max.}$ 3 300, 1 615, 1 589, and 1 505 cm^{-1}; δ 1.21—2.26 (9 H, m, 5-, 6-, 7-, and 8-H_2 and 4a-H), 2.33 (3 H), 2.49—2.76 (2 H, dq, 4-H_2), 4.07 (1 H, s, 8a-H), 7.97 (1 H, d, 6′-H), 8.36 (1 H, dd, 5′-H), 9.12 (1 H, d, 3′-H), and 11.25 (1 H, s, NH); *m/z* 361 (M^+). 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} −18.7, J_{AX} 7.2, and J_{BX} 1.8 Hz, ν_A δ 2.66, and ν_B δ 2.54.

cis-3-*Acetyl*-4a,5,6,7,8,9,10,10a-*octahydro*-4H-*cyclo*-*oct*[e]-1,2-*oxazine* (4j). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and (*Z*)-cyclo-octene (2.2 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (4j) (0.252 g, 60%) as an oil; δ 1.20—1.96 (12 H, m), 2.08—2.48 (3 H, m, 4-H_2 and 4a-H), 2.40 (3 H, MeCO), and 4.12 (1 H, m, 10a-H); the adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 168—169 °C (from chloroform–ethanol) (Found: C, 55.5; H, 5.95; N, 18.2. $C_{18}H_{23}N_5O_5$ requires C, 55.5; H, 5.95; N, 18.0%); $\nu_{max.}$ 3 307, 1 612, and 1 587 cm^{-1}; δ 1.38—2.00 (12 H, m), 2.30 (1 H, m, 4a-H), 2.32 (3 H), 2.48—2.78 (2 H, dq, 4-H_2), 4.18 (1 H, dt, *J* 6.7 and 2.6 Hz, 10a-H), 7.99 (1 H, d, 6′-H), 8.37 (1 H, dd, 5′-H), 9.13 (1 H, d, 3′-H), and 11.27 (1 H, NH); *m/z* 389 (M^+). 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} 7.1, and J_{BX} 3.9 Hz, ν_A δ 2.68, and ν_B δ 2.52.

trans-3-*Acetyl*-4a,5,6,7,8,9,10,10a-*octahydro*-4H-*cyclo*-*oct*-[e]-1,2-*oxazine* (4k). 1-Chlorobutane-2,3-dione 2-oxime (0.31 g, 2.3 mmol) and (*E*)-cyclo-octene [12] (1.1 g, 10 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the oxazine (4k) (0.39 g, 81%), as an oil; δ 1.31—2.13 (14 H, m), 2.33 (3 H, MeCO), 2.52 (1 H, dd, 4-H), and 3.53 (1 H, dq, 10a-H); the adduct was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 192—192.5 °C (from chloroform–ethanol) (Found: C, 55.6; H, 6.1; N, 17.75. $C_{18}H_{23}N_5O_5$ requires C, 55.5; H, 5.95; N, 18.0%); $\nu_{max.}$ 3 300, 1 610, and 1 582 cm^{-1}; δ 1.42—2.10 (13 H, m), 2.17 (1 H, dd, 4-H), 2.32 (3 H), 2.84 (1 H, dd, 4-H), 3.58—3.70 (1 H, dq, *J* 9.7, 6.0, and 3.7 Hz, 10a-H), 7.97 (1 H, d, 6′-H), 8.38 (1 H, dd, 5′-H), 9.13 (1 H, d, 3′-H), and 11.29 (1 H, NH); *m/z* 389 (M^+). 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} −18.6, J_{AX} 4.2, and J_{BX} 12.7 Hz, ν_A δ 2.82, and ν_B δ 2.15.

exo-3-*Acetyl*-4a,5,6,7,8,8a-*hexahydro*-5,8-*methano*-4H-1,2-*benzoxazine* (4l). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and norbornene (0.94 g, 10 mmol) gave the *oxazine* (4l) (0.231 g, 60%), m.p. 34—36 °C (from dichloromethane–hexane) (Found: C, 68.3; H, 7.9; N, 7.4. $C_{11}H_{15}NO_2$ requires 68.4; H, 7.8; N, 7.25%); $\nu_{max.}$ 1 700 and 1 590 cm^{-1}; δ 1.00—1.70 (6 H, m), 1.80—2.00 (2 H, m, 4- and 4a-H), 2.13 (1 H, br, 5-H), 2.42 (3 H), 2.53 (1 H, br, 8-H), 2.99 (1 H, m, 4-H), and 3.58 (1 H, d, *J* 6.9 Hz, 8a-H). The absence of 8-H to 8a-H coupling is indicative of *exo*-stereochemistry.[13]

3-*Acetyl*-6-*ethoxy*-5,6-*dihydro*-4H-1,2-*oxazine* (4m). (With A. K. Yagoub.)[14] 1-Chlorobutane-2,3-dione 2-oxime (1.35 g, 10 mmol) and ethyl vinyl ether (7.2 g, 100 mmol) gave, on evaporation of the solvent followed by distillation, the *oxazine* (4m) (1.40 g, 82%), b.p. 65 °C at 0.01 mmHg (Found: C, 55.6; H, 7.5; N, 7.9. $C_8H_{13}NO_3$ requires C, 56.1; H, 7.6; N, 7.9%); $\nu_{max.}$ 1 690 and 1 585 cm^{-1}; δ 1.16 (3 H, t, *Me*CH_2), 1.64—1.82 (1 H, m, 5-H), 1.95—2.08 (1 H, m, 5-H), 2.15—2.33 (1 H, m, 4-H), 2.33—2.52 (1 H, m, 4-H), 2.40 (3 H, MeCO), 3.66 (1 H, dq, MeC*H*HO), 3.87 (1 H, dq, MeCH*H*O), and 5.20 (1 H, t, *J* 2.8 Hz, 6-H); *m/z* 171 (M^+).

cis-3-*Acetyl*-4a,7a,*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (4n). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and furan (1.36 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)] the *oxazine* (4n) (0.25 g, 75%) as an oil; $\nu_{max.}$ 1 685 and 1 602 cm^{-1}; δ 2.42 (1 H, d, *J* −16.7 Hz, 4-H), 2.45 (3 H), 3.05 (1 H, d, *J* −16.7 Hz, 4-H), 5.12 (1 H, m, 4a-H), 5.19 (1 H, d, 7-H), 5.32 (1 H, 7a-H), and 6.53 (1 H, 6-H); *m/z* 167 (M^+), 150, and 43 (100%). After a few hours at room temperature the furo-oxazine (4n) isomerised to 1-(2-furyl)butane-2,3-dione 2-oxime (7), δ 2.39 (3 H), 3.96 (2 H, CH_2), 6.04 (1 H, d, 3′-H), 6.25 (1 H, dd, 4′-H), 7.26 (1 H, d, 5′-H), and 9.87 (1 H, br, OH); this compound was characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 180—182 °C (from chloroform–ethanol) (Found: C, 48.1; H, 3.7; N, 20.0. $C_{14}H_{13}N_5O_6$ requires C, 48.4; H, 3.25; N, 20.15%).

cis-3-*Acetyl*-4a,6-*dimethyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (4o). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 2,5-dimethylfuran (1.92 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (4o) (0.227 g, 58%), m.p. 32—35 °C (sublimed) (Found: C, 61.35; H, 6.85; N, 7.15. $C_{10}H_{13}NO_3$ requires C, 61.5; H, 6.7; N, 7.2%); $\nu_{max.}$ 1 685 cm^{-1}; δ 1.47 (3 H, 4a-Me), 1.76 (3 H, 6-Me), 2.11 and 3.08 (total 2 H, ABq, *J* −15.2 Hz, 4-H_2), 2.45 (3 H), 4.77 (1 H, 7a-H), and 4.92 (1 H, 7-H); *m/z* 195 (M^+), 178, 152, 96, and 58 (100%); *m** 162.5 (195 ⟶ 178) and 118.5 (195 ⟶ 152).

3-*Acetyl*-4a,9b-*dihydro*-4H-*benzofuro*[2,3-e]-1,2-*oxazine* (4p). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and benzofuran (2.36 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (4p) (0.156 g, 35.5%), m.p. 113—114 °C (from dichloromethane–hexane) (Found: C, 66.6; H, 5.0; N, 6.6. $C_{12}H_{11}NO_3$ requires C, 66.35; H, 5.1; N, 6.45); $\nu_{max.}$ 1 686 cm^{-1}; δ 2.39 (3 H), 2.73 (1 H, dd, 4-H), 2.97 (1 H, dd, 4-H), 5.22 (1 H, ddd, 4a-H), 5.44 (1 H, d, *J* 7.2 Hz, 9b-H), 6.81 (1 H, d, 9-H), 6.98 (1 H, t, 8-H), 7.30 (1 H, t, 7-H), and 7.53 (1 H, d, 6-H); *m/z* 217 (M^+), 200, 175, 157, and 43 (100%); *m** 184.3 (217 ⟶ 200), 141.1 (217 ⟶ 175), and 113.6 (217 ⟶ 157). 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} −16.7, J_{AX} 3.6, and J_{BX} 6.2 Hz, ν_A δ 2.95, ν_B δ 2.73, and ν_X δ 5.20.

The oxazine was stirred in trifluoroacetic acid for 2 h and gave, after work-up, an oil to which the structure 1-(2-benzofuryl)butane-2,3-dione 2-oxime (8) was assigned: δ 2.61 (3 H), 4.12 (2 H), 6.34 (1 H, 3-H), 6.80 (1 H, 4-H), 6.91 (1 H, t,

5-H), 7.16 (1 H, t, 6-H), 7.18 (1 H, d, 7-H), and 7.25 (1 H, br, OH).

6-*Methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine*-3-*carbaldehyde* (5a). 3-Chloro-2-hydroxyiminopropanal (2b) (0.233 g, 1.91 mmol) and α-methylstyrene (2.8 g, 25 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (5a) (0.152 g, 39%), b.p. 115 °C at 0.05 mmHg (Found: C, 71.15; H, 6.5; N, 6.85. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.45; N, 6.9%); $\nu_{max.}$ 1 705 and 1 585 cm^{-1}; δ 1.62 (3 H, 6-Me), 1.65—1.98 (2 H, m, 4-H_2), 2.30—2.49 (2 H, m, 5-H_2), 7.21—7.38 (5 H, m, Ph), and 9.46 (1 H); *m/z* 203 (M^+) and 105 (100%).

A minor product was also isolated (R_F *ca.* 0.3) and was identified by its ^1H n.m.r. spectrum as a 1 : 1 mixture of (*Z*)- and (*E*)-2-hydroxyimino-5-phenylhex-4-enal (0.035 g), the characteristic resonances being, for the *Z*-isomer, δ 2.14 (3 H), 3.44 (2 H, d, 3-H_2), and 5.73 (1 H, t, 4-H), and for the *E*-isomer, δ 2.02 (3 H), 3.21 (2 H, d, 3-H_2), and 5.41 (1 H, t, 4-H); these compounds were not further characterised.

trans-5,6-*Diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine*-3-*carbaldehyde* (5b). 3-Chloro-2-hydroxyiminopropanal (0.856 g, 7 mmol), and (*E*)-stilbene (5 g, 28 mmol) gave, on work-up by p.l.c. [chloroform; then chloroform–ethyl acetate (9 : 1)], the *oxazine* (5b) (0.248 g, 13%), m.p. 130—131 °C (from diethyl ether–pentane) (Found: C, 76.9; H, 5.75; N, 5.0. $C_{17}H_{15}NO_2$ requires C, 76.95; H, 5.7; N, 5.3%); $\nu_{max.}$ 1 688 and 1 583 cm^{-1}; δ 2.60—3.01 (2 H, dABq, 4-H_2), 3.03—3.27 (1 H, dt, 5-H), 4.87 (1 H, d, *J* 9.9 Hz, 6-H), 7.01—7.06 (2 H, m, ArH), 7.17—7.24 (8 H, m, ArH), and 9.70 (1 H); *m/z* 265 (M^+) and 104 (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} −18.9, J_{AX} 5.6, and J_{BX} 11.2 Hz, ν_A δ 2.87, and ν_B δ 2.61.

2-*Hexyl*-5,6-*dihydro*-4H-1,2-*oxazine*-3-*carbaldehyde* (5c). 3-Chloro-2-hydroxyiminopropanal (0.336 g, 2.76 mmol) and oct-1-ene (4.5 g, 40 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1]), the *oxazine* (5c) (0.10 g, 18.5%), b.p. 110 °C at 0.1 mmHg (Found: C, 67.15; H, 9.85; N, 7.35. $C_{11}H_{19}NO_2$ requires C, 66.95; H, 9.7; N, 7.1%); $\nu_{max.}$ 1 703 and 1 585 cm^{-1}; δ 0.91 (3 H, t), 1.25—1.89 (11 H, m), 1.95—2.57 (3 H, m, 4-H_2 and 5-H), 3.85 (1 H, m, 6-H) and 9.50 (1 H); *m/z* 197 (M^+) and 55 (100%).

cis-4a,5,6,7,8,9,10,10a-*Octahydro*-4H-*cyclo-oct*[e]-1,2-*oxazine*-3-*carbaldehyde* (5d). 3-Chloro-2-hydroxyiminopropanal (0.842 g, 6.93 mmol) and (*Z*)-cyclo-octene (7.5 ml, 60 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (5d) (0.566 g, 41.5%), b.p. 145 °C at 0.05 mmHg (Found: C, 67.8; H, 8.85; N, 7.3. $C_{11}H_{17}NO_2$ requires C, 67.65; H, 8.8; N, 7.15%); $\nu_{max.}$ 1 700 and 1 580 cm^{-1}; δ 1.25—2.00 (12 H, m), 2.11—2.47 (2 H, dABq, 4-H_2), 2.23 (1 H, m, 4a-H), 4.22 (1 H, m, 10a-H), and 9.47 (1 H); *m/z* 195 (M^+) and 67 (100%).

cis-4,4a,5,7a-*Tetrahydrocyclopent*[e]-1,2-*oxazine*-3-*carbaldehyde* (5e). 3-Chloro-2-hydroxyiminopropanal (0.425 g, 3.49 mmol) and cyclopentadiene (2.64 g, 40 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (5e) (0.40 g, 76%), b.p. 85 °C at 0.1 mmHg (Found: C, 63.8; H, 6.0; N, 9.55. $C_8H_9NO_2$ requires C, 63.55; H, 6.0; N, 9.25%); $\nu_{max.}$ 1 700 and 1 588 cm^{-1}; δ 2.10—2.27 (2 H, m, 4- and 5-H), 2.54—2.89 (3 H, m, 4-, 4a-, and 5-H), 5.03 (1 H, d, *J* 7.8 Hz, 7a-H), 5.95 (1 H, m, 6-H), 6.16 (1 H, m, 7-H), and 9.59 (1 H); *m/z* 151 (M^+) and 65 (100%).

3-*Ethoxycarbonyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (6a). Ethyl bromopyruvate 2-oxime (3) (0.84 g, 4 mmol) and styrene (2.08 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (6a) (0.049 g, 5%), m.p. 78—79 °C (from diethyl ether–pentane) (Found: C, 66.7; H, 6.5; N, 6.3. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.5; N, 6.0%); $\nu_{max.}$ 1 710 and 1 588 cm^{-1}; δ 1.37 (3 H, t), 1.91—2.31 and 2.42—2.75 (total 4 H, 2 × m, 4- and 5-H_2), 4.36 (2 H, q), 4.84 (1 H, dd, *J* 10.1 and 2.7 Hz, 6-H), and 7.37 (5 H, Ph); *m/z* 233 (M^+) and 142 (100%).

3-*Ethoxycarbonyl*-6-*methyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (6b). Ethyl bromopyruvate 2-oxime (0.42 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* (6b) (0.216 g, 43%), m.p. 71—72 °C (from diethyl ether–pentane) (Found: C, 68.15; H, 7.0; N, 5.85. $C_{14}H_{17}NO_3$ requires C, 68.0; H, 6.95; N, 5.65%); $\nu_{max.}$ 1 713 and 1 595 cm^{-1}; δ 1.27 (3 H, t, *Me*CH_2), 1.54 (3 H, 6-Me), 1.79—1.97 and 2.31—2.56 (total 4 H, 2 × m, 4- and 5-H_2), 4.16—4.33 (2 H, m), and 7.20—7.40 (5 H, m, Ph); *m/z* 247 (M^+), 230, and 77; *m** 214.2 (247 ⟶ 230).

A minor product (R_F 0.3) was also isolated and was identified by its ^1H n.m.r. spectrum as a 1 : 1 mixture of ethyl (*Z*)- and (*E*)-2-hydroxyimino-5-phenylhex-4-enoate, the characteristic resonances being, for the *Z*-isomer, δ 2.12 (3 H), 3.53 (2 H, d, 3-H_2), and 5.76 (1 H, t, 4-H), and for the *E*-isomer, δ 1.99 (3 H), 3.29 (2 H, d, 3-H_2), and 5.43 (1 H, t, 4-H); these compounds were not further characterised.

3-*Ethoxycarbonyl*-6,6-*diphenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (6c). Ethyl bromopyruvate 2-oxime (0.84 g, 4 mmol) and 1,1-diphenylethylene (3.6 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (6c) (0.088 g, 7%), m.p. 124—125 °C (from diethyl ether–pentane) (Found: C, 73.4; H, 6.15; N, 4.65. $C_{19}H_{19}NO_3$ requires C, 73.75; H, 6.2; N, 4.55%); $\nu_{max.}$ 1 705 and 1 600 cm^{-1}; δ 1.32 (3 H, t), 2.37 (2 H, t, 5-H_2), 2.62 (2 H, t, 4-H_2), 4.29 (2 H, q), and 7.23—7.44 (10 H, m, 2 × Ph); *m/z* 309 (M^+), 292, and 77 (100%); *m** 275.9 (309 ⟶ 292).

3-*Ethoxycarbonyl*-6-*hexyl*-5,6-*dihydro*-4H-1,2-*oxazine* (6d). Ethyl bromopyruvate 2-oxime (0.42 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)], the oxazine (6d) (0.013 g, 2.5%) as an oil; $\nu_{max.}$ 1 725 and 1 596 cm^{-1}; δ 0.89 (3 H, t), 1.20—1.85 (13 H, m), 1.93—2.70 (4 H, m, 4- and 5-H_2), 3.77 (1 H, m, 6-H), and 4.33 (2 H, q); *m/z* 241 (M^+) and 119 (100%); the sample was not further characterised.

cis-3-*Ethoxycarbonyl*-4,4a,5,9b-*tetrahydroindeno*[2,1-e]-1,2-*oxazine* (6e). Ethyl bromopyruvate 2-oxime (0.84 g, 4 mmol) and indene (4.64 g, 40 mmol) gave, on work-up by layer p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (6e) (0.525 g, 53.5%), b.p. 160 °C at 0.05 mmHg (Found: C, 68.3; H, 6.4; N, 5.8. $C_{14}H_{15}NO_3$ requires C, 68.55; H, 6.15; N, 5.7%); $\nu_{max.}$ 1 715 and 1 595 cm^{-1}; δ 1.34 (3 H, t), 2.10—2.25 (1 H, dd, 4-H), 2.72—2.90 (3 H, m, 4-, 4a-, and 5-H), 3.09—3.23 (1 H, dd, 5-H), 4.32 (2 H, q), 5.19 (1 H, d, *J* 6.0 Hz, 9b-H), 7.20—7.30 (3 H, m, ArH), and 7.46—7.51 (1 H, d, 9-H); *m/z* 245 (M^+) and 114 (100%).

cis-3-*Ethoxycarbonyl*-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (6f). Ethyl bromopyruvate 2-oxime (0.84 g, 4 mmol) and cyclopentadiene (2.64 g, 40 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (6f) (0.62 g, 79%), b.p. 135 °C at 0.08 mmHg (Found: C, 61.75; H, 6.95; N, 6.9. $C_{10}H_{13}NO_3$ requires C, 61.5; H, 6.7; N, 7.2%); $\nu_{max.}$ 1 720 and 1 590 cm^{-1}; δ 1.38 (3 H, t), 2.16—2.32 (2 H, m, 4- and 4a-H), 2.62—2.94 (3 H, m, 4-H, and 5-H_2), 4.36 (2 H, q), 4.96 (1 H, d, 7a-H), 5.86 (1 H, m, 6-H), and 6.11 (1 H, m, 7-H); *m/z* 195 (M^+) and 105 (100%).

cis-3-*Ethoxycarbonyl*-5-*isopropylidene*-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (6g). Ethyl bromopyruvate 2-oxime (0.84 g, 4 mmol) and 6,6-dimethylfulvene (1.0 g) gave, on work-up by p.l.c. [hexane–diethyl ether (1 : 1)], the *oxazine* (6g) (0.35 g, 37%), b.p. 145 °C at 0.05 mmHg (Found: C, 66.6; H, 7.45; N, 5.7. $C_{13}H_{17}NO_3$ requires, C, 66.35; H, 7.3;

N, 5.95%); $\nu_{max.}$ 1 720 and 1 595 cm^{-1}; δ 1.36 (3 H, t), 1.78 (6 H), 2.26 and 2.80 (total 2 H, dABq, J −14.7, 8.0, and 8.0 Ha, 4-H_2), 3.35 (1 H, q, 4a-H), 4.35 (2 H, mq), 5.21 (1 H, d, J 9.8 Hz, further split, 7a-H), 5.89 (1 H, d, 7-H), and 6.63 (1 H, d, 6-H); m/z 235 (M^+) and 91 (100%).

3-*Ethoxycarbonyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (6h). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and furan (1.36 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxazine* (6h) (0.183 g, 46.5%), m.p. 75—77 °C (from diethyl ether–pentane) (Found: C, 54.9; H, 5.45; N, 7.3. $C_9H_{11}NO_4$ requires C, 54.8; H, 5.6; N, 7.1%); $\nu_{max.}$ 1 720 and 1 607 cm^{-1}; δ 1.31 (3 H, t), 2.55 (1 H, dd, 4-H), 3.04 (1 H, dd, 4-H), 4.33 (2 H, dq), 5.08—5.19 (2 H, m, 4a- and 7-H), 5.25—5.33 (1 H, dd, J 7.0 and 2.8 Hz, 7a-H), and 6.54 (1 H, d, 6-H); m/z 197 (M^+), 180, 152, 124, and 68; m^* 164.5 (197 ⟶ 180), 128.4 (180 ⟶ 154), and 101.2 (152 ⟶ 124). 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} −15.6, J_{AX} 4.8, and J_{BX} 5.9 Hz, ν_A δ 3.07, and ν_B δ 2.60.

On heating the oxazine (6h) at 100 °C for 1 h, quantitative isomerisation occurred to give ethyl 3-(2-furyl)-2-hydroxyiminopropionate as an oil; δ 1.31 (3 H, t), 4.01 (2 H, s, CH_2), 4.31 (2 H, q), 6.09 (1 H, d, 3′-H), 6.27 (1 H, m, 4′-H), 7.29 (1 H, d, 5′-H), and 9.75 (1 H, br, s, OH).

Ethyl 2-*hydroxyimino*-3-(*pyrrol*-2-*yl*)*propionate* (9a) *and its pyrrol*-3-*yl isomer* (10a). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and pyrrole (1.34 g, 20 mmol), gave on work-up by p.l.c. [chloroform–ethyl acetate (1 : 1)], a mixture of two isomers, *ethyl* 2-*hydroxyimino*-3-(*pyrrol*-2-*yl*)*propionate* (9a) and *ethyl* 2-*hydroxyimino*-3-(*pyrrol*-3-*yl*)*propionate* (10a) (0.216 g, 55%), in the ratio 86 : 14. Recrystallisation of the mixture did not alter the isomer ratio, m.p. 118—120 °C (from dichloromethane–hexane) (Found: C, 54.9; H, 6.25; N, 14.4. $C_9H_{12}N_2O_3$ requires C, 55.1; H, 6.15; H, 14.3%); $\nu_{max.}$ 3 380br, 3 250br, 1 712, and 1 551 cm^{-1}; the ^1H n.m.r. spectrum of the mixture indicated the presence of the two isomers; for the ester (9a), δ 1.30 (3 H, t), 3.91 (2 H), 4.28 (2 H, q), 6.01—6.12 (2 H, m, 3′- and 4′-H), 6.63 (1 H, m, 5′-H), 8.61 (1 H, br, NH), and 10.32 (1 H, br, OH); for the ester (10a), δ 1.30 (3 H, t), 3.81 (2 H), 4.28 (2 H, q), 6.16 (1 H, m, 4′-H), 6.63 (2 H, m, 2′- and 5′-H), 8.05 (1 H, br, NH), and 10.32 (1 H, br, OH); m/z 196 (M^+), 179, and 80 (100%); m^* 163.5 (196 ⟶ 179).

Ethyl 2-*hydroxyimino*-3-(N-*methylpyrrol*-2-*yl*)*propionate* (9b) *and its* (N-*methylpyrrol*-3-*yl*) *isomer* (10b). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and *N*-methylpyrrole (1.62 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (1 : 1)], a mixture of two isomers, *ethyl* 2-*hydroxyimino*-3-(N-*methylpyrrol*-2-*yl*)*propionate* (9b) and *ethyl* 2-*hydroxyimino*-3-(N-*methylpyrrol*-3-*yl*)*propionate* (10b) (0.226 g, 53.5%), in the ratio 80 : 20. Recrystallisation of the mixture did not alter the isomer ratio, m.p. 98—101 °C (from dichloromethane–hexane) (Found: C, 57.15; H, 6.6; N, 13.2. $C_{10}H_{14}N_2O_3$ requires C, 57.15; H, 6.7; N, 13.35%); $\nu_{max.}$ 3 210br, 1 728, and 1 712 cm^{-1}; the ^1H n.m.r. spectrum of the mixture indicated the presence of the two isomers; for the ester (9b), δ 1.31 (3 H, t), 3.61 (3 H), 3.91 (2 H), 4.28 (2 H, q), 5.96—6.05 (2 H, m, 3′- and 4′-H), 6.52 (1 H, m, 5′-H), and 10.30 (1 H, br, OH); for the ester (10b), δ 1.31 (3 H, t), 3.55 (3 H), 3.79 (2 H), 4.28 (2 H, q), 6.06 (1 H, m, 4′H), 6.46—6.55 (2 H, m, 2′- and 5′-H), and 10.30 (1 H, OH); m/z 210 (M^+), 193, and 94 (100%); m^* 177.4 (210 ⟶ 193).

1-(*Indol*-3-*yl*)*butane*-2,3-*dione* 2-*oxime* (11a). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and indole (2.35 g, 20 mmol) gave, on work-up by p.l.c. [chloroform; then chloroform–ethyl acetate (4 : 1)], the *oxime* (11a) (0.316 g, 73%), m.p. 120—121 °C (from dichloromethane–hexane) (Found: C, 66.4; H, 5.5; N, 12.7. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.6; N, 12.95%); $\nu_{max.}$ 3 420, 3 245s, and 1 688 cm^{-1}; δ [$(CD_3)_2SO$] 2.30 (3 H), 3.87 (2 H), 6.95 (1 H, t, 5′-H), 7.03 (1 H, t, 6′-H), 6.99 (1 H, 2′-H), 7.29 (1 H, d, 4′-H), 7.63 (1 H, d, 7′-H), 10.59 (1 H, br, NH), and 12.18 (1 H, OH); m/z 216 (M^+), 199, 172, and 130 (100%); m^* 183.3 (216 ⟶ 199) and 148.7 (199 ⟶ 172).

Ethyl 2-*hydroxyimino*-3-(*indol*-3-*yl*)*propionate* (11b). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and indole (1.2 g, 10 mmol) gave, after p.l.c. [chloroform–hexane (1 : 1)], the oxime (11b) (0.407 g, 82.5%), m.p. 155—157 °C (from dichloromethane) (lit.,[15] 156—157 °C) (Found: C, 63.15; H, 5.85; N, 11.6. Calc. for $C_{13}H_{14}N_2O_3$: C, 63.4; H, 5.75; N, 11.4%); $\nu_{max.}$ 3 420br and 1 721 cm^{-1}; δ [$(CD_3)_2SO$] 1.18 (3 H, t), 3.94 (2 H), 4.17 (2 H, q), 7.00 (1 H, t, 5′-H), 7.08 (1 H, t, 6′-H), 7.10 (1 H, 2′-H), 7.37 (1 H, d, 4′-H), 7.63 (1 H, d, 7′-H), 10.86 (1 H, NH), and 12.33 (1 H, OH); m/z 246 (M^+), 229, and 130 (100%); m^* 213.2 (246 ⟶ 229).

1-(2-*Methylindol*-3-*yl*)*butane*-2,3-*dione* 2-*oxime* (11c). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 2-methylindole (2.62 g, 20 mmol) gave, on work-up by p.l.c. [chloroform; then chloroform–ethyl acetate (4 : 1)], the *oxime* (11c) (0.30 g, 65%), m.p. 177—180 °C (from ethanol–hexane) (Found: C, 67.8; H, 6.35; N, 12.3. $C_{13}H_{14}N_2O_2$ requires C, 67.8; H, 6.15; N, 12.15%); $\nu_{max.}$ 3 380br and 1 674 cm^{-1}; δ [$(CD_3)_2SO$] 2.25 (3 H), 2.41 (3 H), 3.81 (2 H), 6.88 (1 H, t, 5′-H), 6.93 (1 H, t, 6′-H), 7.18 (1 H, d, 4′-H), 7.52 (1 H, d, 7′-H), 10.33 (1 H, br, NH), and 12.12 (1 H, OH); m/z 230 (M^+) and 144 (100%).

3-*Acetyl*-4a-*methyl*-4,4a,9,9a-*tetrahydro*-1,2-*oxazino*[6,5-b]-*indole* (12a). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 3-methylindole (2.62 g, 20 mmol) gave, on work-up by p.l.c. [chloroform; then chloroform–ethyl acetate (4 : 1)], the *oxazine* (12a) (0.40 g, 86%), m.p. 93—95 °C (from diethyl ether–pentane) (Found: C, 67.7; H, 6.2; N, 12.45. $C_{13}H_{14}N_2O_2$ requires C, 67.8; H, 6.15; N, 12.15%); $\nu_{max.}$ 3 405, 1 686, and 1 602 cm^{-1}; δ 1.42 (3 H), 2.24 (1 H, d, J −15.4 Hz, 4-H), 2.28 (3 H), 3.20 (1 H, d, J −15.4 Hz, 4-H), 4.88 (1 H, br, NH), 5.31 (1 H, 9a-H), 6.60 (1 H, d, 5-H), 6.73 (1 H, t, 6-H), 6.99 (1 H, d, 8-H), and 7.04 (1 H, t, 7-H); m/z 230 (M^+), 213, and 43 (100%); m^* 197.3 (230 ⟶ 213).

3-*Ethoxycarbonyl*-4a-*methyl*-4,4a,9,9a-*tetrahydro*-1,2-*oxazino*[6,5-b]*indole* (12b). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and 3-methylindole (2.62 g, 20 mmol) gave, on work-up by column chromatography [chloroform; then chloroform–ethyl acetate (4 : 1)], the *oxazine* (12b) (0.426 g, 81.5%), m.p. 70—71 °C (from diethyl ether–pentane) (Found: C, 64.85; H, 6.25; N, 10.85. $C_{14}H_{16}N_2O_3$ requires C, 64.6; H, 6.2; N, 10.75%); $\nu_{max.}$ 3 415br, 1 705, and 1 606 cm^{-1}; δ 1.35 (3 H, t), 1.42 (3 H), 2.43 (1 H, d, J −15.9 Hz, 4-H), 3.15 (1 H, d, J −15.9 Hz, 4-H), 4.24 (2 H, dq), 5.03 (1 H, br, NH), 5.29 (1 H, 9a-H), 6.57 (1 H, d, 5-H), 6.73 (1 H, t, 6-H), 7.01 (1H, t, 7-H), and 7.02 (1 H, d, 8-H); m/z 260 (M^+), 243, and 131 (100%); m^* 227.1 (260 ⟶ 243).

1-(2,4-*Dimethoxyphenyl*)*butane*-2,3-*dione* 2-*oxime* (13a) *and its* 2,6-*dimethoxyphenyl isomer* (14a). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 1,3-dimethoxybenzene (2.76 g, 20 mmol), gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of two isomers, 1-(2,4-*dimethoxyphenyl*)*butane*-2,3-*dione* 2-*oxime* (13a) and 1-(2,6-*dimethoxyphenyl*)*butane*-2,3-*dione* 2-*oxime* (14a) (0.30 g, 63%), in the ratio 82 : 18. Recrystallisation of the mixture did not alter the isomer ratio, m.p. 78—90 °C (from dichloromethane–hexane) (Found: C, 60.6; H, 6.3; N, 6.0. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max.}$ 3 410br, 1 670, and 1 612 cm^{-1}; the ^1H n.m.r. spectrum of the mixture indicated the presence of the two isomers; for the oxime (13a), δ 2.38 (3 H), 3.76 (6 H), 3.81 (2 H), 6.33—6.43 (2 H, m, 3′- and 5′-H), 6.93

(1 H, d, 6'-H), and 9.21 (1 H, br, OH); for the oxime (14a), δ 2.38 (3 H), 3.76 (6 H), 3.90 (2 H), 6.50 (2 H, d, 3'- and 5'-H), 7.12 (1 H, t, 4'-H), and 8.74 (1 H, br, OH); *m/z* 237 (M^+).

3-(2,4-*Dimethoxyphenyl*)-2-*hydroxyiminopropanal* (13b) *and its* 2,6-*dimethoxyphenyl isomer* (14b). 3-Chloro-2-hydroxyiminopropanal (0.411 g, 3.38 mmol) and 1,3-dimethoxybenzene (2.76 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], a mixture of two isomers, 3-(2,4-*dimethoxyphenyl*)-2-*hydroxyiminopropanal* (13b) and 3-(2,6-*dimethoxyphenyl*)-2-*hydroxyiminopropanal* (14b) (0.314 g, 41.5%), in the ratio 79 : 21; b.p. 165 °C at 0.05 mmHg (Found: C, 59.25; H, 6.0; N, 6.05. $C_{11}H_{13}NO_4$ requires C, 59.2; H, 5.85; N, 6.3%); $\nu_{max.}$ 3 350br, 1 700, and 1 610 cm^{-1}; the ^1H n.m.r. spectrum of the mixture showed the presence of the two isomers; for the isomer (13b), δ 3.72 (6 H), 3.74 (2 H), 6.32—6.41 (2 H, m, 3'- and 5'-H), 6.94 (1 H, d, 6'-H), 9.47 (1 H), and 10.30 (1 H, br, OH); for the isomer (14b), δ 3.72 (6 H), 3.80 (2 H), 6.48 (2 H, d, 3'- and 5'-H), 7.14 (1 H, t, 4'-H), 9.43 (1 H), and 10.30 (1 H, br, OH); *m/z* 223 (M^+).

Ethyl 3-(2,4-*dimethoxyphenyl*)-2-*hydroxyiminopropionate* (13c) *and its* 2,6-*dimethoxyphenyl isomer* (14c). Ethyl bromopyruvate 2-oxime (0.42 g, 2 mmol) and 1,3-dimethoxybenzene (2.76 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (3 : 2)], a mixture of two isomers, the esters (13c) and (14c) (0.06 g, 11%) in the ratio 82 : 18. Trituration of the oily product with diethyl ether gave a white solid, m.p. 84—86 °C (from diethyl ether–pentane); $\nu_{max.}$ 3 220br, 1 713, and 1 610 cm^{-1}; the ^1H n.m.r. spectrum showed the presence of the two isomers; for the ester (13c), δ 1.30 (3 H, t), 3.78 (6 H), 3.90 (2 H), 4.28 (2 H), 6.38—6.45 (2 H, m, 3'- and 5'-H), 7.04 (1 H, d, 6'-H), and 10.25 (1 H, br, OH); for the ester (14c), δ 1.30 (3 H, t), 3.78 (6 H), 3.98 (2 H), 4.28 (2 H, q), 6.53 (2 H, d, 3'- and 5'-H), 7.16 (1 H, t, 4'-H), and 9.78 (1 H, br, OH); *m/z* 267 (M^+); these products were not further characterised.

1-(2,5-*Dimethoxyphenyl*)*butane*-2,3-*dione* 2-*oxime* (15). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 1,4-dimethoxybenzene (2.76 g, 20 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxime* (15) (0.040 g, 8.5%), m.p. 100—101 °C (from dichloromethane–hexane) (Found: C, 60.85; H, 6.55; N, 6.05. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max.}$ 3 370, 1 672, and 1 600 cm^{-1}; δ 2.39 (3 H), 3.73 (3 H), 3.77 (3 H), 3.87 (2 H), 6.65—6.80 (3 H, m, ArH), and 8.28 (1 H, br, OH); *m/z* 237 (M^+).

1-(2-*Dimethylaminophenyl*)*butane*-2,3-*dione* 2-*oxime* (16) *and its* 4-*dimethylaminophenyl isomer* (17). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and *NN*-dimethylaniline (2.42 g, 20 mmol) gave, on work-up by p.l.c. [hexane–diethyl ether (3 : 2)], a mixture of the oximes (16) and (17) (0.076 g, 17%) in the ratio 70 : 30; for the oxime (16), δ 2.42 (3 H), 2.77 (6 H), 3.87 (2 H), 7.10—7.31 (4 H, m, ArH), and 10.5 (1 H, br, OH); for the oxime (17), δ 2.36 (3 H), 2.91 (6 H), 3.82 (2 H), 6.68 (2 H, d, 3'- and 5'-H), 7.45 (2 H, d, 2'- and 6'-H), and 10.5 (1 H, br, OH); *m/z* 220 (M^+); the mixture was not further characterised.

1-(2-*Hydroxy*-1-*naphthyl*)*butane*-2,3-*dione* 2-*oxime* (18a). 1-Chlorobutane-2,3-dione 2-oxime (0.271 g, 2 mmol) and 2-naphthol (1.44 g, 10 mmol) gave, on work-up by p.l.c. [chloroform–ethyl acetate (19 : 1)], the *oxime* (18a) (0.099 g, 20%), m.p. 137—140 °C (from dichloromethane–hexane) (Found: C, 68.65; H, 5.3; N, 5.55. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.75%); $\nu_{max.}$ 3 170br, 1 667, and 1 593 cm^{-1}; the ^1H n.m.r. spectrum [$(CD_3)_2SO$] showed an equilibrium between the oxime (18a) and its cyclic tautomer (18b) in the ratio 63 : 37; δ 1.73 [1.1 H, Me of (18b)] and 2.27 [1.9 H, MeCO of (18a)]; δ 3.72 and 4.24 [0.74 H, ABq, CH_2 of (18b)] and 4.09 [1.26 H, CH_2 of (18a)]; δ 7.08—7.92 (6 H, m, ArH), and 10.60—12.96 (br, OH); *m/z* 243 (M^+).

3-*Acetyl*-4,6-*dimethyl*-6-*phenyl*-5,6-*dihydro*-4H-1,2-*oxazine* (21). 4-Choropentane-2,3-dione 3-oxime [10] (0.3 g, 2 mmol) and α-methylstyrene (2.24 g, 19 mmol) gave the oxazine (21) (0.198 g, 42%) as a yellow oil, shown by ^1H n.m.r. spectroscopy to be a mixture of two isomers (4- and 5-H *cis* and 4- and 5-H *trans*) in the ratio 89 : 11; the characteristic resonances being, major component, δ 0.71 (3 H, d, 4-Me), 1.55 (3 H, 6-Me), 2.42 (3 H), 2.77 (1 H, sextet, 4-H); minor component, δ 1.13 (3 H, d, 4-Me), 1.57 (3 H, 6-Me), 2.33 (3 H, s, MeCO), and 2.55—2.65 (1 H, m, 4-H); treatment of the mixture with 2,4-dinitrophenylhydrazine, followed by recrystallisation, gave the 2,4-*dinitrophenylhydrazone* of the major isomer, m.p. 182—185 °C (from chloroform–ethanol) (Found: C, 58.15; H, 5.15; N, 16.9. $C_{20}H_{21}N_5O_5$ requires C, 58.4; H, 5.15; N, 17.0%).

A by-product was also isolated in the above reaction, and was shown to be *pent*-4-*ene*-2,3-*dione* 3-*oxime* (20), (0.07 g, 30%), m.p. 32—34 °C (sublimed) (Found: C, 53.05; H, 6.1; N, 12.15. $C_5H_7NO_2$ requires C, 53.1; H, 6.25; N, 12.4%); $\nu_{max.}$ 3 320br and 1 690 cm^{-1}; δ 2.42 (3 H), 5.79 (1 H, dd, *J* 12.2 and 2.2 Hz, *cis* 5-H), 6.37 (1 H, dd, *J* −18.0 and 2.2 Hz, *trans* 5-H), 6.73 (1 H, dd, *J* −18.0 and 12.2 Hz, 4-H), and 9.56 (1 H, br, OH); *m/z* 113 (M^+).

3-*Acetyl*-4-*methyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (22). 4-Chloropentane-2,3-dione 3-oxime (0.3 g, 2 mmol) and furan (1.36 g, 20 mmol) gave 3-*acetyl*-4-*methyl*-4a,7a-*dihydro*-4H-*furo*[2,3-e]-1,2-*oxazine* (22) (0.173 g, 48%), as an oil, shown by ^1H n.m.r. spectroscopy to be a mixture of two isomers (*exo* 4-H and *endo* 4-H) in the ratio 92 : 8; b.p. 154 °C at 0.02 mmHg (Found: C, 59.8; H, 6.15; N, 7.6. $C_9H_{11}NO_3$ requires C, 59.65; H, 6.1; N, 7.75%); $\nu_{max.}$ 1 705 and 1 614 cm^{-1}; δ 1.12 (2.76 H, d, *J* 7.8 Hz, 4-Me major component), 1.18 (0.24 H, d, *J* 7.8 Hz, 4-Me minor component), 2.42 (0.24 H), 2.45 (0.08 H, m, 4-H minor), 2.46 (2.76 H), 3.43 (0.92 H, quintet, 4-H major), 4.72 (1 H, t, *J* 7.8 Hz, 4a-H), 4.91 (1 H, dd, *J* 7.8 and 2.6 Hz, 7a-H), 5.26 (1 H, t, *J* 2.6 Hz, 7-H), and 6.76 (1 H, d, *J* 2.6 Hz, 6-H); *m/z* 181 (M^+). The oxime (20) (45%) was also isolated.

Competitive Cycloaddition to the Oxime (2a).*—A solution of 1-chlorobutane-2,3-dione 2-oxime (1 mmol) and two olefins (each 5 mmol) in dichloromethane (50 cm^3) was stirred with sodium carbonate (1 g) for 24 h. The reaction mixture was then filtered and the filtrate was evaporated to remove the solvent and the excess of the olefins. The residues were analysed by ^1H n.m.r. spectroscopy. Results are given in the Introduction.

* Reaction carried out by Dr. D. E. Davies.

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