Thermal and Acid-catalysed Rearrangements of 5,6-Dihydro-4*H*-1,2-oxazines

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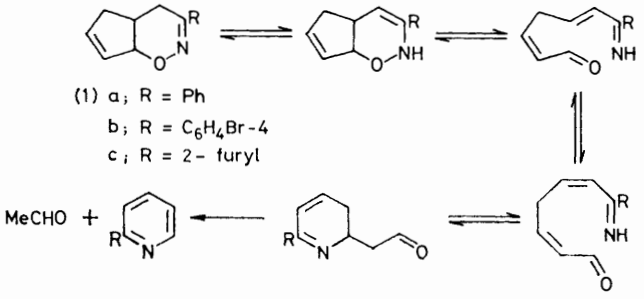
2-Arylpyridines have been isolated in good yields from the pyrolysis of 3-arylcyclopent[*e*]oxazines (1) in the melt above 200 °C; a mechanism is proposed for this reaction which involves tautomerism of the 4*H*- to 2*H*-oxazines, followed by cleavage of the N–O bond. A similar ring-opening occurs with the benzo-derivative (3). The oxazines are methylated at nitrogen by methyl fluorosulphonate and methylation facilitates the ring-opening.

Acid-catalysed rearrangement of the cyclopent[*e*]oxazine (1a) takes a different course, giving the spiro-isomer (9) by cleavage of the C–O bond. Similarly, the furo-oxazine (2) is cleaved in acid to give α-(2-furyl)acetophenone oxime, which is further transformed into *cis*-3-(3-phenylisoxazol-5-yl)prop-2-enol (10a) in trifluoroacetic acid. Acid-catalysed ring-opening of 6-morpholino-3,6-diphenyl-5,6-dihydro-4*H*-1,2-oxazine (16) results in the formation of the *syn* and *anti* mono-oximes of 1,4-diphenylbutane-1,4-dione.

In the preceding paper we described a method of preparing several 5,6-dihydro-4*H*-1,2-oxazines.[1] This heterocyclic system has hitherto been rather inaccessible, and its chemistry has not been explored.[2] We



Scheme 1

considered that by exploiting the inherent weakness of the N–O bond in these compounds, we might use them as precursors of other heterocyclic and acyclic systems. For this reason we have investigated the thermal and acid-catalysed reactions of several 5,6-dihydro-4*H*-1,2-oxazines, and have delineated the major reaction pathways of these compounds.

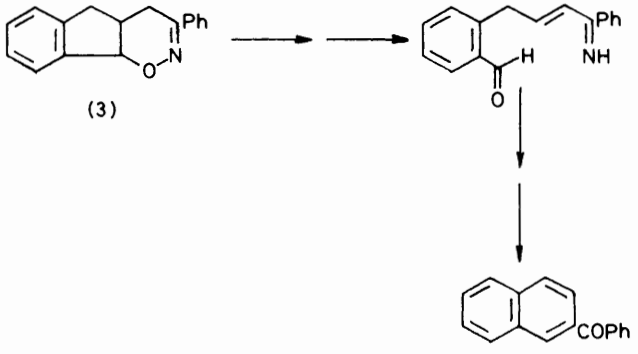
Results and Discussion

Thermolysis.[3]—The cyclopent[*e*]-1,2-oxazines (1) were found to be unstable above *ca.* 200 °C. The thermal decomposition of the oxazine (1a) was carried out by heating a molten specimen at 250 °C for 10 min in a bulb-to-bulb distillation apparatus. During the decomposition acetaldehyde was detected, both by smell and by the development of a blue colour when a filter paper impregnated with a mixture of morpholine and sodium nitroprusside was exposed to the vapour.[4] The major product distilled over into the second bulb during the thermolysis and it was purified by redistillation. It was identified as 2-phenylpyridine from its n.m.r. spectrum and from the m.p. of its picrate; the yield of redistilled product was 80%. Analogous results were obtained with the oxazines (1b) and (1c): acetaldehyde was detected, and the corresponding 2-arylpyridines were isolated. The oxazine (1b) decomposed smoothly at 200—210 °C to give 2-(4-bromophenyl)pyridine in good yield as a crystalline solid, but the oxazine (1c) required a higher temperature (270—280 °C) and the yield of the pyridine was lower (40%).

We also pyrolysed these oxazines in solution, and in the vapour phase at 400—600 °C, but the reactions gave mixtures and we were unable to identify the products. The furo-oxazine (2) also gave a complex mixture of products when pyrolysed in the melt. The indeno-oxazine (3) decomposed at 200 °C in the melt to give a mixture from which 2-naphthyl phenyl ketone was isolated (32%) by chromatography.

A route by which the 2-arylpyridines could be formed from the oxazines is shown in Scheme 1. The first step is the conversion of the 4*H*-oxazines into the 2*H*-isomers; these can then undergo electrocyclic ring-opening, isomerisation of the double bond, re-cyclisation, and aromatisation. Electrocyclic ring-opening of 2*H*-1,2-oxazines has been shown by Eschenmoser and his co-workers to take place very readily, in a manner analogous to that shown in Scheme 1.[5]

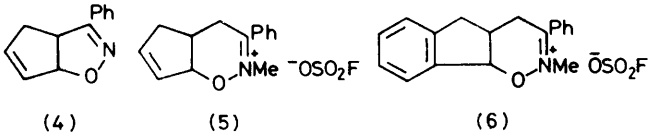
A very similar sequence can account for the formation of 2-naphthyl phenyl ketone from the oxazine (3); this is outlined in Scheme 2. In this case the intermediate aldehyde is aromatic; the naphthalene system can be generated by an aldol condensation of the aldehydic



Scheme 2

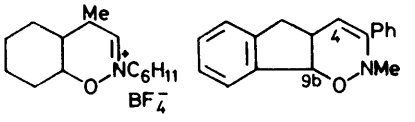
carbonyl group and the activated methylene group in the adjacent side-chain. It is possible that the cyclisation occurs on the silica support used to separate the reaction products.

An alternative scheme for these reactions was considered in which the initial step was homolysis of the N–O bond of the 4*H*-oxazines. This seems a less likely route because we found that the isoxazoline (4), which



(4) (5) (6)

has a structure similar to that of the oxazine (1a) but with the N–O bond in a five-membered ring, was unaffected by heating in the melt at 240—250 °C. More direct evidence for the intermediacy of 2*H*-oxazines in the reactions was sought by attempting to promote the interconversion of the 4*H*- and 2*H*-tautomers. The addition of strong acids caused a completely different reaction to occur, which is described later. However, the oxazines (1a) and (3) combined readily with methyl fluorosulphonate to form stable salts, which are formulated as the *N*-methyl derivatives (5) and (6) on the basis of their n.m.r. spectra. These salts are structurally very similar to the *N*-alkyloxazinium salts, such as (7), which Eschenmoser and his co-workers have isolated



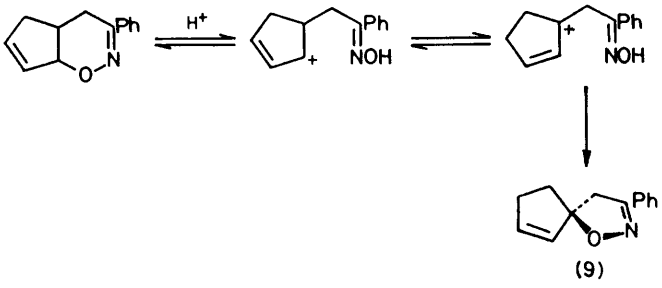
(7) (8)

from the reaction of *N*-alkyl-*N*-vinylnitrosonium salts with alkenes, and, like compound (7), they react readily with bases such as sodium carbonate and triethylamine. The products from both (5) and (6) with these bases were oils which decomposed on attempted purification. The ^{1}H n.m.r. spectrum of the crude product from (6) was consistent with the 2*H*-oxazine structure (8): it showed an *N*-methyl signal at δ 2.94 and one-hydrogen doublets at δ 5.18 and 5.61 which can be assigned to signals from the hydrogen atoms at C-9b and C-4, respectively. When heated with ethanolic hydrochloric acid this oil gave 2-naphthyl phenyl ketone (36%), probably by a route analogous to that shown in Scheme 2.

A similar sequence of reactions, involving the *N*-methylation and base-catalysed ring-opening of 3-methyl-5,6-dihydro-4*H*-1,2-oxazine, has recently been described.[6] The reaction appears to be a general one for 4*H*-1,2-oxazines.

Acid-catalysed Rearrangements.—The reaction of the oxazine (1a) was originally explored with the intention of bringing about a Beckmann rearrangement; however, this was not observed, neither were products isolated which could have resulted from a 4*H*- →2*H*-oxazine rearrangement. The oxazine (1a) was recovered after being heated in ethanolic hydrochloric acid, and after being set aside in trifluoroacetic acid at room temperature for 12 h. When it was heated in formic acid or in trifluoroacetic acid, an isomeric compound was isolated in moderate yield. This was assigned the spiro-structure (9) on the basis of its ^{1}H n.m.r. spectrum. The methylene group in the heterocyclic ring appears as a simple AB doublet (*J* 17 Hz); the unsymmetrical position of the double bond in the carbocyclic ring is deduced from the separate signals for the olefinic hydrogen atoms, and from the appearance of the signals for the other four alicyclic hydrogen atoms as multiplets in a 1 : 2 : 1 ratio.

This rearrangement probably results from protonation of the oxazine (1a) at oxygen, followed by opening of the

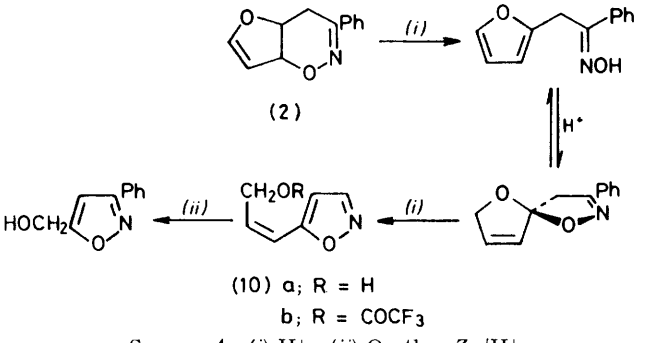


(9)

SCHEME 3

heterocyclic ring. The resulting carbocation may then isomerise in the acidic medium to give a more stable ion which is both allylic and tertiary, as shown in Scheme 3. This can then give the spiro-compound (9) by recyclisation.

A similar type of ring-opening takes place when the furo-oxazine (2) is treated with acid, although the conditions are much milder. The oxazine (2) was converted into α-(2-furyl)acetophenone oxime when it was heated in dioxan containing a few drops of hydrochloric acid: the structure of the product was confirmed by an independent synthesis involving a Darzens reaction with furfuraldehyde.



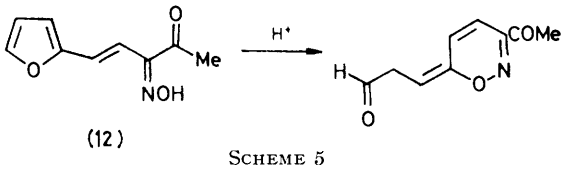
(2)

(10) a; R = H
b; R = $COCF_3$

SCHEME 4 (*i*) H^+; (*ii*) O_3, then Zn/H^+

A different product was isolated from the reaction of the oxazine (2) with trifluoroacetic acid at room temperature. The product, which was isolated in 69% yield after chromatography, was identified as the isoxazole (10a). The structure was established by ozonolysis to give the known alcohol (11), a specimen of which was synthesised by the literature procedure [7] for comparison. The *cis* configuration of the double bond in (10a) was deduced from the coupling constant (*J* 11.6 Hz) of the olefinic hydrogen atoms in the n.m.r. spectrum. The

reaction mixture before chromatography contained the isoxazole in the form of its trifluoroacetic acid ester (10b), and this could be isolated as a crystalline solid after removal of the acid by distillation.

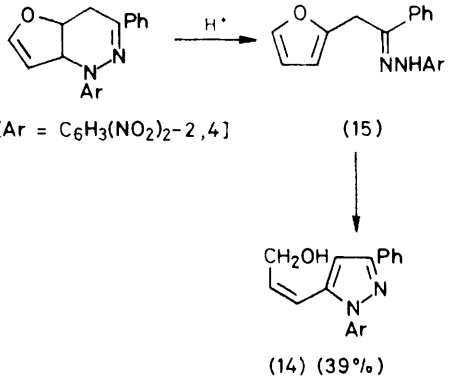


(12)

SCHEME 5

The isoxazole (10) is a secondary product, which is derived from α-(2-furyl)acetophenone oxime by further transformation in acid. This was shown by dissolving the oxime in trifluoroacetic acid; after 21 h compound (10a) was isolated in 80% yield. The sequence of reactions, starting from the oxazine (2), is shown in Scheme 4. The sequence is very similar to that we have suggested to occur with the oxazine (1a) (Scheme 3), except that the intermediate oxime can be isolated, and the spiro-compound to which it rearranges cannot, since it reacts further in acid.

The acid-catalysed rearrangement of furans containing nucleophilic side-chains is probably a much more general reaction than the isolated example reported here might indicate, although no systematic studies of such reactions have been made. An example which is probably mechanistically similar is the acid-catalysed rearrangement of the oxime (12) shown in Scheme 5, which was reported in 1918.[8] We have also found that the pyrazine (13) rearranges in an analogous manner to that of the oxazine (2) in trifluoroacetic acid to give the pyrazole (14), presumably by way of the intermediate furan (15) (Scheme 6).



(13) [Ar = $C_6H_3(NO_2)_2$-2,4] (15)

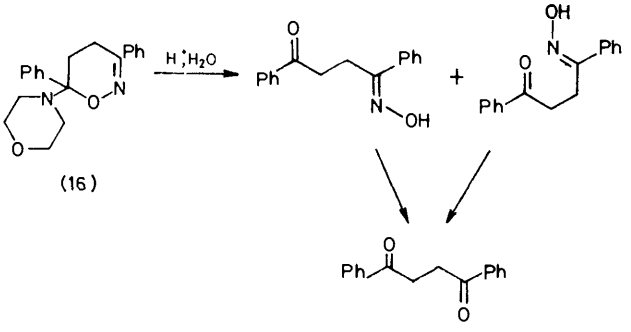
(14) (39%)

SCHEME 6

Other 4*H*-1,2-oxazines which are readily available by cycloaddition are those derived from enamines. As an example of these, we investigated the acid-catalysed ring-opening of the oxazine (16). Predictably this was cleaved in mild conditions to give a mixture of the *syn* and *anti* mono-oximes of 1,4-diphenylbutane-1,4-dione; in more vigorous conditions the diketone itself was isolated (Scheme 7). Such reactions are potentially useful as routes to other 1,4-dicarbonyl compounds.[9]

One other example of the acid-catalysed cleavage of a 4*H*-1,2-oxazine has been described previously: 5-amino-5,6-dihydro-3,5-diphenyl-4*H*-1,2-oxazine was reported to be cleaved at the C–O bond, to give 2,4-diphenylpyrrole.[10]

In summary, we have shown that some 4*H*-1,2-oxazines are thermally labile and that they react by cleavage of the N–O bonds, probably by way of the 2*H*-oxazine tautomers. The oxazines can be alkylated at nitrogen and the alkylation provides an alternative to *N*-vinylnitrosonium ion cycloaddition as a route to 2*H*-oxazine derivatives. The usefulness of this alternative ultimately depends upon the range of olefins to which nitrosoalkenes will add in reasonable yields, and we are currently attempting to define this range. All the acid-catalysed reactions which we have observed involve



(16)

SCHEME 7

cleavage of a C–O bond, and this may allow some selectivity to be developed in the synthetic uses of these oxazines.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained at 220 MHz in $CDCl_3$, except where indicated otherwise. Mass spectra were recorded at 70 eV using a direct insertion probe. Preparative layer chromatography was carried out with silica gel GF_{254} (Merck) as the stationary phase. The oxazines were prepared as described in the preceding paper.[1]

Thermolysis of Oxazines.—(*a*) 3-*Phenyl*-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (1a). The oxazine (0.2 g, 1.0 mmol) was heated at 250 °C for 10 min in a bulb-to-bulb distillation apparatus. Acetaldehyde was detected at the open end of the apparatus by its smell and by a spot test using morpholine and sodium nitroprusside.[4] A yellow liquid distilled into the collecting bulb, and this was redistilled at 160 °C and 15 mmHg. The product was characterised as 2-phenylpyridine (0.125 g, 80%) by conversion into its picrate, m.p. 176—178 °C (lit.,[11] 175 °C).

(*b*) 3-(4-*Bromophenyl*)-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (1b). The oxazine (0.3 g, 1.1 mmol) was heated at 210 °C for 10 min and the product was isolated by distillation at 200 °C and 15 mmHg to give 2-(4-bromophenyl)-pyridine (0.197 g, 78%), m.p. 63—65 °C (lit.,[12] 61—62 °C) picrate m.p. 165 °C (lit.,[12] 164 °C).

(*c*) 3-(2-*Furyl*)-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazine* (1c). The oxazine (0.2 g, 1.1 mmol) was heated at 270—280 °C for 10 min. The product was isolated by distillation at 140 °C and 15 mmHg and was identified

as 2-(2-furyl)pyridine (0.061 g, 40%), picrate m.p. 170—174 °C (lit.,[13] 171—174 °C).

(*d*) 3-*Phenyl*-4,4a,5,9b-*tetrahydroindeno*[2,3-e]-1,2-*oxazine* (3). The oxazine (0.1 g, 0.4 mmol) was heated at 200 °C for 10 min. T.l.c. of the product [chloroform–ethyl aetate (19 : 1)] gave 2-naphthyl phenyl ketone (0.03 g, 32%), m.p. 80—82 °C (lit.,[14] 82 °C), which was identical (i.r., mixed m.p. 80—82 °C) to a specimen prepared by the literature method.

Attempted Thermolysis of 3-*Phenyl*-4,6a-*dihydro*-3aH-*cyclopent*[d]*isoxazole* (4).—The isoxazoline was prepared, in improved yield, by a modification of the literature method. Benzhydroximoyl chloride (0.40 g, 2.56 mmol) was dissolved in ether (10 cm^3) and the solution was added dropwise during 1 h to a stirred solution of cyclopentadiene (1 cm^3, 12.2 mmol) and triethylamine (0.5 cm^3, 3.6 mmol) in ether (5 cm^3). T.l.c. [chloroform–ethyl acetate (49 : 1)] gave the isoxazoline (0.439 g, 93%), m.p. 47 °C (lit.,[15] 47—48 °C). The isoxazoline was unchanged after being heated in the melt at 240—250 °C for 15 min.

2-*Methyl*-3-*phenyl*-4,4a,5,7a-*tetrahydrocyclopent*[e]-1,2-*oxazinium Fluorosulphonate* (5).—Methyl fluorosulphonate (0.06 cm^3, 0.7 mmol) and the oxazine (1a) (0.10 g, 0.5 mmol) were stirred together in dry ether (10 cm^3) at 20 °C for 3 h. The white precipitate which formed was filtered off, washed with ether, and dried to give the *oxazinium salt* (5) (0.113 g, 72%), m.p. 111—114 °C (decomp.) (from dichloromethane–ether) (Found: C, 53.5; H, 4.9; N, 4.2. $C_{14}H_{16}FNO_4S$ requires C, 53.7; H, 5.2; N, 4.5%); $\nu_{max.}$ 1 630w and 1 280s cm^{-1}; δ 2.30—2.45 (1 H, m), 2.76—3.10 (2 H, m), 3.34—3.55 (2 H, m), 3.93 (3 H), 5.84—5.97 (2 H, m), 6.37 (1 H, m), 7.60—7.70 (3 H, m), and 7.73—7.80 (2 H, m); *m/e* 213 ($[C_{14}H_{15}NO]^+$), 196, and 118 (base).

2-*Methyl*-3-*phenyl*-4,4a,5,9b-*tetrahydroindeno*[2,3-e]-1,2-*oxazinium Fluorosulphonate* (6).—Methyl fluorosulphonate (0.07 cm^3, 0.9 mmol) and the oxazine (3) (0.20 g, 0.8 mmol) were stirred in dry benzene (10 cm^3) at 20 °C for 18 h. The colourless precipitate was filtered off, washed with benzene, and dried to give the *oxazinium salt* (6) (0.174 g, 60%), m.p. 128—133 °C (from dichloromethane–hexane) (Found: C, 59.3; H, 5.3; N, 3.8. $C_{18}H_{18}FNO_4S$ requires C, 59.5; H, 5.0; N, 3.9%); $\nu_{max.}$ 1 630w, 1 595w, and 1 280s cm^{-1}; δ 2.90—3.10 (2 H, m), 3.33—3.70 (3 H, m), 3.90 (3 H), 6.30 (1 H, m), 7.25—7.46 (4 H, m), and 7.50—7.70 (5 H, m); *m/e* 263 ($[C_{18}H_{17}NO]^+$), 246, 244, and 84 (base).

Reaction of the Oxazinium Salt (6) *with Sodium Carbonate*.—The oxazinium salt (0.10 g, 0.4 mmol) and anhydrous sodium carbonate (0.30 g, 2.8 mmol) were stirred in dichloromethane (10 cm^3) at 0 °C for 0.5 h. The suspension was filtered and the colourless filtrate was washed with water, dried, and solvent evaporated off to leave a yellow oil. The n.m.r. spectrum (60 MHz) of the oil included the following signals: δ 2.91 (3 H, N-Me), 5.18 (1 H, d, *J* 4.5 Hz, H-9b), and 5.61 (1 H, d, *J* 4 Hz, H-4). The oil decomposed when chromatographic purification was attempted; it was therefore dissolved in ethanolic hydrochloric acid and the solution was heated under reflux for 2 h. The solvent was removed and t.l.c. of the residue gave 2-naphthyl phenyl ketone (0.230 g, 36%), m.p. 80—82 °C.

3-*Phenyl*-2-*aza*-1-*oxaspiro*[4.4]*nona*-2,6-*diene* (9).— The oxazine (1a) (0.10 g, 0.5 mmol) was dissolved in formic acid (10 cm^3) and the solution was heated under reflux for 2 h. The solvent was removed and the residue was partitioned between chloroform and water. The organic phase was dried and evaporated to dryness; t.l.c. of the residue [chloroform–ethyl acetate (19 : 1)] gave the *spiro-compound* (9) (0.039 g, 39%), m.p. 76—77 °C (from pentane) (Found: C, 78.4; H, 6.7; N, 7.3. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%); δ 2.00—2.20 (1 H, m), 2.35—2.50 (2 H, m) 2.55—2.70 (1 H, m), 3.26 (1 H, d, *J* 17 Hz), 3.41 (1 H, d, *J* 17 Hz), 5.83 (1 H, m), 6.10 (1 H, m), 7.36—7.50 (3 H, m), and 7.60—7.76 (2 H, m); *m/e* 199 (M^+), 182, 167, 165, and 80 (base).

The same product was isolated (23%) when the oxazine (1a) was heated in trifluoroacetic acid for 24 h.

α-(2-*Furyl*)*acetophenone Oxime*.—(*a*) *From the oxazine* (2). The oxazine (2) (0.109 g, 0.54 mmol) was dissolved in dioxan (15 cm^3) containing 2 drops of concentrated hydrochloric acid, and the solution was heated under reflux for 30 min. T.l.c. of the product [chloroform–ethyl acetate (19 : 1)] gave α-(2-furyl)acetophenone oxime (0.039 g, 36%), m.p. 85—87 °C (from hexane) (lit.,[16] 90 °C). The compound was identical to a specimen prepared by route (*b*).

(*b*) *From furfuraldehyde*. Ethyl α-chlorophenylacetate (15 g, 0.076 mol) and furfuraldehyde (6.3 cm^3, 0.076 mmol) were dissolved in absolute ethanol (10 cm^3). The solution was rapidly stirred and cooled in ice while sodium ethoxide solution [from sodium (1.7 g, 0.074 g atom) and ethanol (30 cm^3)] was added dropwise during 3 h. The solution was stirred for a further 12 h, then the solvent was removed and the residue was taken up in ether (50 cm^3) and 1N HCl (30 cm^3). The ethereal solution was washed, dried and evaporated to dryness to leave crude ethyl 3-(2-furyl)-2-phenylprop-2-enoate 2,3-epoxide as an oil which decomposed when distillation was attempted. The ester (7.6 g) was dissolved in a cold solution of sodium hydroxide (1.4 g) in water (10 cm^3) and ethanol (5 cm^3). After 5 min the solution was acidified and extracted with ether. Column chromatography (silica; chloroform) gave α-(2-furyl)-acetophenone as an oil (0.99 g, 18%). The oxime, prepared (47%) from the ketone in the standard way, had m.p. 88—90 °C (from hexane); mixed m.p. 85—89 °C with a specimen prepared by route (*a*).

cis-3-(3-*Phenylisoxazol*-5-*yl*)*prop*-2-*enol* (10a) *and its Trifluoroacetate* (10b).—(*a*) *From the oxazine* (2). The oxazine (0.055 g, 0.27 mmol) was allowed to stand in trifluoroacetic acid solution at 20 °C for 18 h. The acid was then distilled off and t.l.c. of the residue [alumina; chloroform–ethyl acetate (19 : 1)] gave the *isoxazole* (10a) (0.035 g, 64%), m.p. 95—96 °C (from dichloromethane–hexane) (Found: C, 71.9; H, 5.5; N, 7.0. $C_{12}H_{11}NO_2$ requires C, 71.6; H, 5.5; N, 7.0%); $\nu_{max.}$ 3 300 cm^{-1} (OH); δ 2.95 (1 H, signal disappears when solution shaken with D_2O), 4.74 (2 H, dd, *J* 6.0 and 1.7 Hz), 6.20 (1 H, dt, *J* 11.6 and 6.0 Hz), 6.40 (1 H, dt, *J* 11.6 and 1.7 Hz), 6.46 (1 H), 7.40—7.56 (3 H, m), and 7.73—7.85 (2 H, m); *m/e* 201 (M^+) and 172 (base). Crystallisation of the reaction mixture directly after removal of the acid gave the *trifluoroacetate* (10b) of this alcohol, m.p. 100—102 °C (from carbon tetrachloride–hexane) (Found: C, 57.1; H, 3.6; N, 4.8. $C_{14}H_{10}F_3NO_3$ requires C, 56.6; H, 3.4; N, 4.7%); $\nu_{max.}$ 1 770s cm^{-1} (CO); δ 5.45 (2 H, dd, *J* 6.4 and 2.2 Hz), 6.05 (1 H, dt, *J* 12.2 and 6.4 Hz), 6.58 (1 H, dt, *J* 12.2 and 2.2 Hz), 6.57 (1 H), 7.45—7.55 (3 H, m), and 7.80—7.88 (2 H, m); *m/e* 297 (M^+) and 200. The ester was readily hydrolysed to the alcohol (10a) in the presence of a catalytic amount of alumina.

(*b*) *From* α-(2-*furyl*)*acetophenone oxime*. A solution of

the oxime (0.1 g, 0.50 mmol) in trifluoroacetic acid (5 cm^3) was set aside at 20 °C for 21 h. This gave the alcohol (10a) (0.08 g, 80%) after chromatography on alumina.

Ozonolysis of the Isoxazole Alcohol (10a).—The isoxazole (0.1 g, 0.5 mmol) in dichloromethane (25 cm^3) was treated with an excess of ozone; the solvent was then removed and the residue was reduced with zinc dust in acetic acid at room temperature for 12 h. This gave 5-hydroxymethyl-3-phenylisoxazole (0.028 g, 32%), m.p. 50—52 °C (lit.,[7] 50—52 °C), which was identical (mixed m.p. 50—52 °C) to a specimen prepared by the literature method.

cis-3-[1-(2,4-*Dinitrophenyl*)-3-*phenylpyrazol*-5-*yl*]*prop*-2-*enol* (14).— 1-(2,4-Dinitrophenyl)-3-phenyl-1,4,4a,7a-tetrahydrofuro[3,2-*c*]pyridazine (13) [1] (0.20 g, 0.55 mmol) was dissolved in trifluoroacetic acid (20 cm^3) and the solution was stirred at 20 °C. The reaction mixture became dark and after 2 h the acid was removed by distillation. The residue was dissolved in dichloromethane and pentane was added to precipitate the *pyrazole* (14) (0.078 g, 39%), m.p. 144—146 °C (Found: C, 59.1; H, 3.8; N, 15.2. $C_{18}H_{14}N_4O_5$ requires C, 59.0; H, 3.9; N, 15.3%); $\nu_{max.}$ 3 450 cm^{-1} (OH); δ(CD_3CN) 1.93 (1 H, signal disappears when solution shaken with D_2O), 4.41 (2 H, dd, *J* 5.4 and 1.5 Hz), 6.05 (1 H, dt, *J* 12.2 and 5.4 Hz), 6.22 (1 H, dt, *J* 12.2 and 1.5 Hz), 6.86 (1 H), 7.35—7.50 (3 H, m), 7.76—7.90 (3 H, m), 8.55 (1 H, dd, *J* 9 and 3 Hz), and 8.77 (1 H, d, *J* 3 Hz); *m/e* 366 (M^+).

1,4-*Diphenylbutane*-1,4-*dione Mono-oximes*.—6-Morpholino-3,6-diphenyl-5,6-dihydro-4*H*-1,2-oxazine (16) was prepared *in situ* from α-chloroacetophenone oxime (0.2 g, 1.18 mmol) and α-morpholinostyrene.[1] The crude product was suspended and stirred in ethanolic hydrochloric acid (5 cm^3 2N HCl in 50 cm^3 ethanol) at 20 °C for 2.5 h. T.l.c. of the product [chloroform–ethyl acetate (9 : 1)] gave (at R_F 0.3) anti-1,4-*diphenylbutane*-1,4-*dione mono-oxime* (0.095 g, 32%), m.p. 118—119 °C (from ethanol) (Found: C, 75.7; H, 6.1; N, 5.6. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); $\nu_{max.}$ 3 240br (OH) and 1 680 (CO) cm^{-1}; δ (100 MHz) 3.24 (4 H), 7.27—7.47 (6 H, m), 7.56—7.69 (2 H, m), and 7.87—7.99 (2 H, m); *m/e* 253 (M^+), 236, and 148 (base). A band at R_F 0.2 gave syn-1,4-*diphenylbutane*-1,4-*dione mono-oxime* (0.098 g, 33%), m.p. 125—128 °C (from ethanol) (Found: C, 75.7; H, 5.9; N, 5.7%); $\nu_{max.}$ 3 350 (sharp, OH), and 1 660 (CO) cm^{-1}; δ (100 MHz) 2.97 (br, 4 H), 7.38 (br, 6 H), and 7.50—7.90 (br, 4 H); *m/e* 253 (M^+), 236, and 148 (base).

When a similar experiment was performed but the solution was heated under reflux for 2 h before chromatography, the product was 1,4-diphenylbutane-1,4-dione (0.159 g, 57%), m.p. 145—147 °C (from carbon tetrachloride) (lit.,[14] 145 °C).

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