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The Formation of Dihydrohydroxyspiro[1,2]oxazines from the Reaction of Fischer's Base with Some Isonitroso Compounds. A Multinuclear NMR Study

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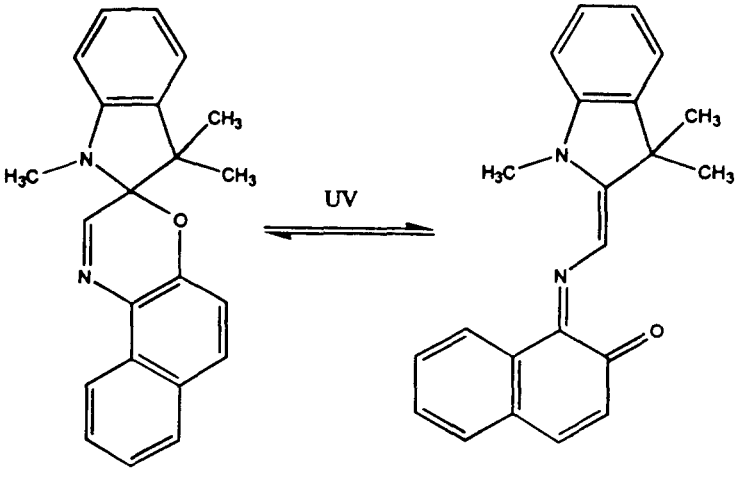
ABSTRACT

Attempts to prepare photochromic spiro[1,4]oxazines ***5a–5c*** *by the reaction of isonitroso compounds* ***4a–4c*** *with Fischer's base led instead to the 1,3,3-trimethylspiro[indoline-2,6'-[4'H]-5',6'-dihydro-4'-hydroxy-1,2-oxazines]* ***7a–7c****. In each case, a multinuclear NMR study confirmed that the products were mixtures of the two possible diastereoisomers. The isomer ratio was found to change over a period of time. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

Organic photochromic materials have been the subject of intense recent investigation due to their wide variety of potential applications, which include ophthalmic and sunglass lenses, optical recording and solar energy storage.[1–4] In particular, spirooxazines have emerged as a class of organic photochromes of particular interest due to their ability to impart intense photo-colouration in appropriate application media and to provide relatively good photo-fatigue resistance. For example, 1,3,3-trimethylspiro[indoline-2,3'-[4H]naphth[2,1-b][1,4]oxazine] (**1**) is essentially colourless in solution, but when exposed to UV light, the solution acquires an intense blue colour. When the light source is removed the solution once again becomes colourless.[5] UV light absorption by the spirooxazine (**1**) causes cleavage of the relatively weak spiro carbon–oxygen bond with the formation of a coloured merocyanine structure such as **2**.



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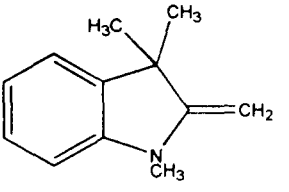
When the light source is removed, compound **2** reverts to the spirooxazine **1** by a thermally-induced ring-closure reaction. In general, the synthesis of spirooxazines is relatively straightforward. Usually this involves the reaction of an o-nitrosohydroxy aromatic compound with an alkylidene heterocycle, commonly 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (**3**).



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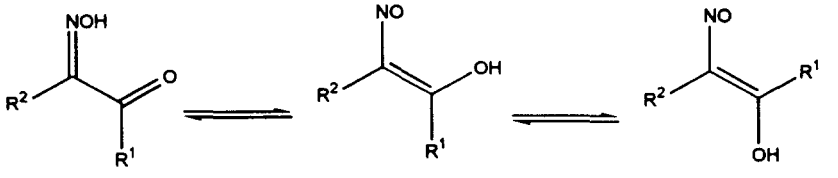
For example, compound **1** is obtained from the reaction of Fischer's base with 1-nitroso-2-naphthol.[5] In this paper we report on attempts to prepare spiro-1,4-oxazines from some non-aromatic isonitroso compounds with a view to extending the shade range of this type of photochromic derivative.

RESULTS AND DISCUSSION

There are no previous reports of attempts to prepare photochromic spirooxazines from non-aromatic nitrosohydroxy compounds. For example,

the isonitroso compounds **4a–4c** might in principle be expected to react with Fischer's base to produce the spirooxazines **5a–5c**, respectively.



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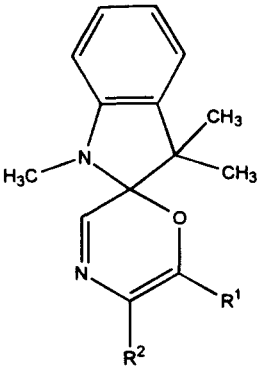

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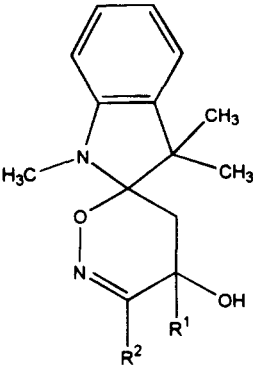

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Compound	R^1	R^2
a	CH_3	$CONHC_6H_5$
b	CH_3	$CO_2C_2H_5$
c	C_6H_5	H

In a previous paper, we demonstrated that the results of PPP molecular orbital calculations, after refinement by parameter optimisation, could provide

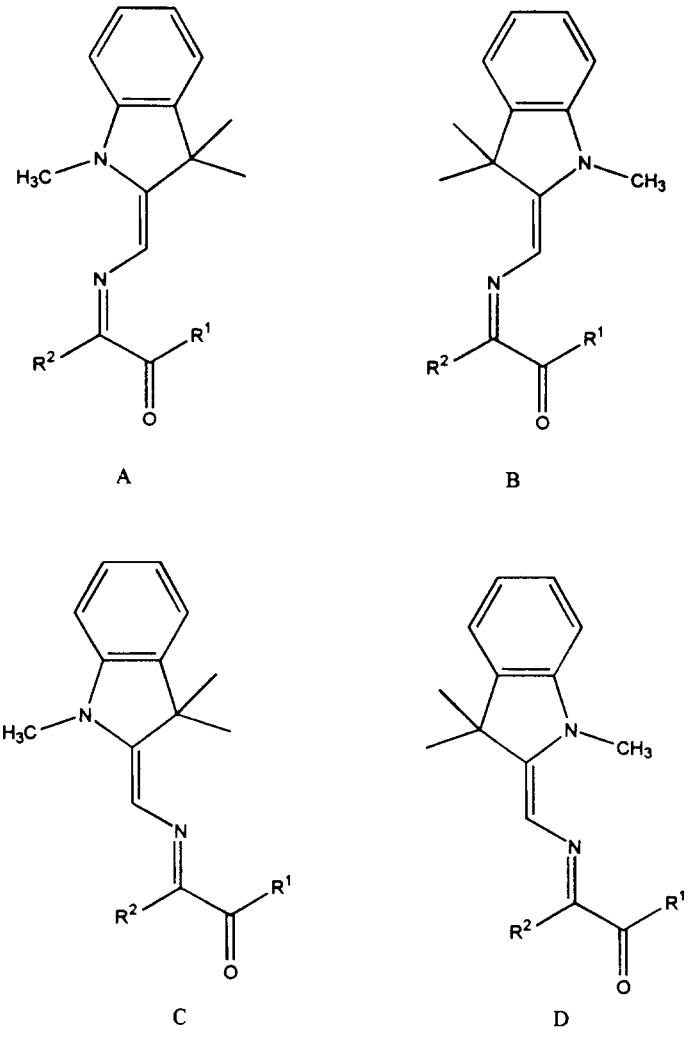


Fig. 1. Geometrical isomers A–D of merocyanines **6a–6c**.

a reasonable account of the experimental λ_{max} values for the ring-opened photomerocyanine forms of a range of spirooxazines, although precise interpretation of the results is complicated by the possibility of a number of geometrical isomers.[6] The results of PPP MO calculations for the four transoid isomers A–D of the merocyanines **6a–6c** (Fig. 1), which might be derived from ring opening of compounds **5a–5c**, are given in Table 1. These merocyanines are predicted to be significantly hypsochromic with respect to compound **2** (588 nm),[5,6] and consequently of interest with a view to extending the range of red photochromic materials of this type.[7] In addition,

TABLE 1
Calculated Electronic Spectral Data for Isomers A–D (Fig. 1) of Merocyanines **6a–6c**

Compound	*Calculated* λ_{max}/nm (f_{osc})			
	A	*B*	*C*	*D*
6a	491 (1.00)	481 (1.02)	485 (0.89)	473 (0.90)
6b	499 (1.05)	488 (1.04)	506 (1.06)	497 (1.06)
6c	472 (0.74)	456 (0.74)	466 (0.78)	453 (0.87)

the oscillator strength values suggest that the compounds might be expected to show a high intensity of colour.

Treatment of compounds **4a–4c** with Fischer's base (**3**), however, failed to give spiro-1,4-oxazines **5a–5c**. Instead, the reactions led to the 1,3,3-tri-

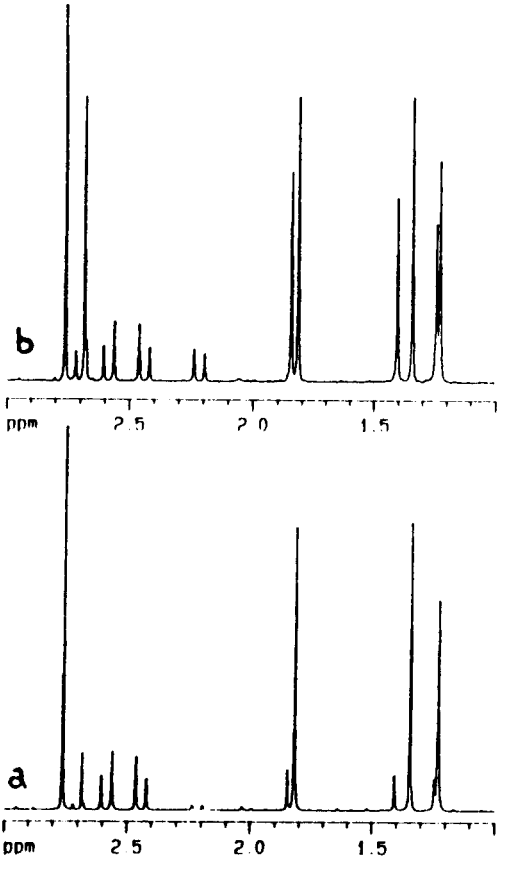
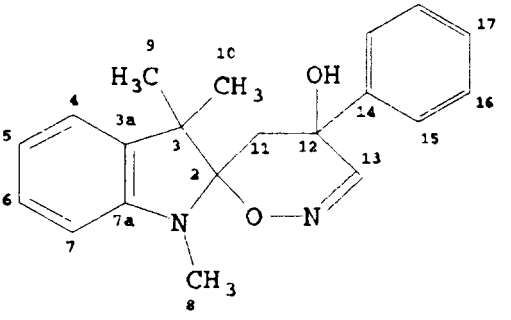


Fig. 2. Part of the ^1H NMR spectrum of compound **7a** in deuteriochloroform (a) recorded immediately after dissolving and (b) after several days.

methylspiro[indoline-2,6′-[4′H]-5′,6′-dihydro-4′-hydroxy-1,2-oxazines] **7a–7c** in moderate yields. In each case, NMR spectral evidence confirms that the products are mixtures of the two diastereoisomers possible as a result of the presence of two chiral centres in the molecules. Attempts to separate the

TABLE 2

^{1}H, ^{13}C and ^{15}N Chemical Shifts of the Two Diastereoisomers (**I**) and (**II**) of Compound **7a** in Deuteriochlorofom



	I[a]		*II*[a]	
C/H	*δ(¹H)*	*δ(¹³C)*	*δ(¹H)*	*δ(¹³C)*
2	—	108.61	—	108.90
3	—	46.70	—	47.35
3a	—	136.38	—	136.34
4	6.96	119.96	6.98	[b]
5	6.79	119.47	6.79	[b]
6	7.12	127.63	7.13	127.51
7	6.48	105.88	6.49	105.78
7a	—	148.79	—	148.90
8	2.77	28.20	2.69	[c]
9,10	1.24	28.44	1.25	[c]
	1.35	19.46	1.42	19.32
11	2.45,2.59[d]	37.53	2.26,2.75[d]	36.23
12	[e]	74.74	[f]	74.57
13	—	137.74	—	137.23
14	1.83	28.26	1.85	[c]
15	[g]	156.76	[h]	156.66
16	—	136.60	—	136.69
17	7.58	120.39	7.58	120.32
18	7.23	128.71	7.23	128.71
19	7.05	124.78	7.05	124.71
N—CH_3		−302.1[i]		−306.6[i]
CONH		−247.5[i]		−247.8[i]
N—O		−72.7[i]		−71. 01[i]

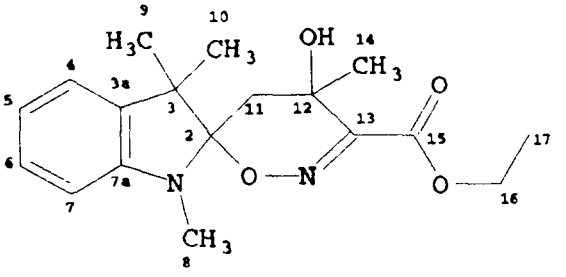
[a] **I**:**II** ratio immediately after dissolving = 1:0.1; **I**:**II** ratio after several days standing = 1:0.8; [b] 120.27 or 119.47; [c] 28.51, 28.35 or 28.30; [d] prochiral CH_2 group; [e] δ(OH) = 4.06; [f] δ(OH) = 3.76; [g] δ(CONH) = 11.89; [h] δ(CONH) = 11.78; [i] δ(^{15}N).

isomers using a range of chromatographic techniques were unsuccessful. The NMR spectra also demonstrated that the isomer ratio changed over a period of time, as is illustrated in Fig. 2.

The structures of compounds **7a–7c** were deduced from a detailed investigation of their spectral properties. The mass spectra of the compounds in each case showed the appropriate molecular ions (see Experimental). NMR spectral data for compounds **7a–7c** are given in Tables 2–4, respectively. In the interest of clarity, the atomic numbering scheme given in the accompanying figures was used, rather than that based on systematic

TABLE 3

^{1}H and ^{13}C Chemical Shifts of the Two Diastereoisomers (**I**) and (**II**) of Compound **7b** in Deuteriochloroform



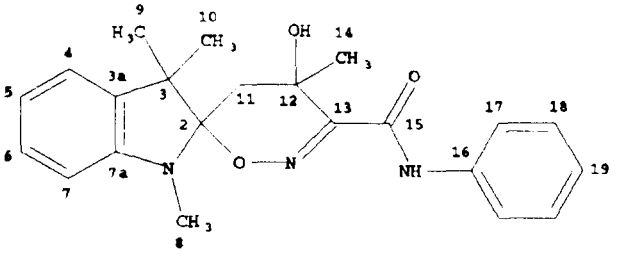
	I[a]		*II*[a]	
C/H No.	*δ(¹H)*	*δ(¹³C)*	*δ(¹H)*	*δ(¹³C)*
2	—	108.86	—	109.21
3	—	46.98	—	47.21
3a	—	136.46	—	136.42
4	6.91	119.05	6.93	119.02
5	6.73	119.93	6.73	120.35
6	7.06	127.36	7.07	127.31
7	6.43	105.74	6.46	105.71
7a	—	149.08	—	149.18
8	2.80	28.32	2.71	28.28
9,10	1.24	28.49	1.26	28.66
	1.33	19.39	1.41	19.84
11	2.45,2.60[b]	37.54	2.23,2.70[b]	36.38
12	[c]	74.24	[d]	73.91
13	—	133.47	—	132.88
14	1.701	28.20	1.704	28.54
15	—	160.35	—	160.13
16	4.31	61.44	4.36,4.26[b]	61.36
17	1.31	13.93	1.31	13.98

[a] **I:II** ratio immediately after dissolving = 1:0.1; **I:II** ratio after several days standing = 1:0.95; [b] prochiral CH_2 group; [c] δ(OH) = 3.50; [d] δ(OH) = 3.20.

nomenclature. Compound **7a** gives rise to two sets of signals in its ^1H (Fig. 2), ^{13}C and ^{15}N NMR spectra, corresponding to the existence of the two diastereoisomers. There are two types of acidic proton in the ^1H NMR spectrum: $\delta_H(OH)$ = 4.06 and 3.76; $\delta_H(CONH)$ = 11.89 and 11.78. The ^{15}N chemical shifts due to the $CONHC_6H_5$ groups (δ_N = −247.5 and −247.8) in the reaction product (**7a**) are very similar to that in the starting isonitroso compound (**4a**) (δ_N = −242.5 in DMSO).[8] $^1J(^{15}N, ^1H)$ coupling constants in both diastereoisomers of compound **7a** are 88.8 Hz. These data, together with the presence of a carbonyl stretching vibration at 1671 cm^{-1} in the infrared spectrum, provide evidence that the $CONHC_6H_5$ group remains unchanged as a result of the reaction. A signal due to a ketone carbonyl group (δ_c = 194.81)[8] is given by the starting isonitroso compound **4a**, but there is no comparable signal given by the reaction product (**7a**). In edited DEPT spectra, signals due to methylene groups were found (δ_c = 37.77 and 36.40), corresponding to one in each of the two diastereoisomers. The arrangement of CH_2 groups in the environment (–C–CH_2–C(OH)–) was

TABLE 4

^1H Chemical Shifts of the Two Diastereoisomers (**I**) and (**II**) of Compound **7c** in Hexadeuteriodimethyl Sulfoxide



C/H No.	*I*[a] *δ(¹H)*	*II*[a] *δ(¹H)*
4	6.95	7.02
5	6.69	6.71
6	7.05	7.07
7	6.51	6.54
8	2.90	2.71
9,10	1.04	1.27
	1.29	1.58
11	2.63,2.83[b]	2.48,2.88[b]
13	7.19	7.10
15	7.53	7.52
16	7.48	7.48
17	7.38	7.38

[a] **I**:**II** ratio 1:1.5; [b] prochiral CH_2 group.

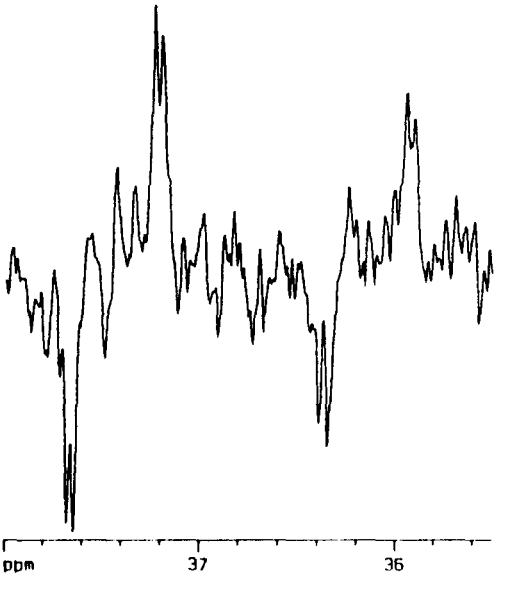


Fig. 3. Part of the 1D INADEQUATE spectrum (CH_2 group) of compound **7a** in deuteriochloroform.

confirmed by measurement of the one-dimensional (1D) INADEQUATE (Incredible Natural Abundance DoublE QUAntum Transfer Experiment) spectrum.[9,10] The INADEQUATE technique is based on the measurement of J(C,C) coupling constants. The principle disadvantage of this type of measurement is the extremely low sensitivity, because only 1 in approximately 10000 molecules (due to the 1.1% natural abundance of the ^{13}C nucleus) contains the ^{13}C–^{13}C pair required for the observation of signals. As Fig. 3 illustrates, the CH_2 groups of both diastereoisomers provide two ^1J(C,C) coupling constants, confirming that the methylene carbon is attached to two other carbons. Further evidence for the existence of the (–O–N=) arrangement is provided by the significant upfield shift of the signal due to this nitrogen in compound **7a** (δ_N = −71.0 and −72.7) compared with that in the spectrum of the starting isonitroso compound **4a** (δ_N = +17.5 ppm).[8] A similar trend is observed, for example, for δ_N from $Me_2C{=}NOH$ (δ_N = 52) compared with $Me_2C{=}NOCH_3$ (δ_N = 12).[11] Further, the δ_c signals due to C-2 are at 108.61 and 108.90 ppm, typical of an aliphatic carbon attached to two heteroatoms. In Fischer's base (**3**), the δ_c signal due to the corresponding carbon is found at 162.2.[12] The δ_N signals due to the indoline ring in the isomers of compound **7a** are at −302.1 and −306.6 ppm. The previously unreported ^{15}N NMR spectrum of Fischer's base (**3**) was measured and a value of δ_N = −283.8 ppm in $CDCl_3$ was obtained. Similar spectral

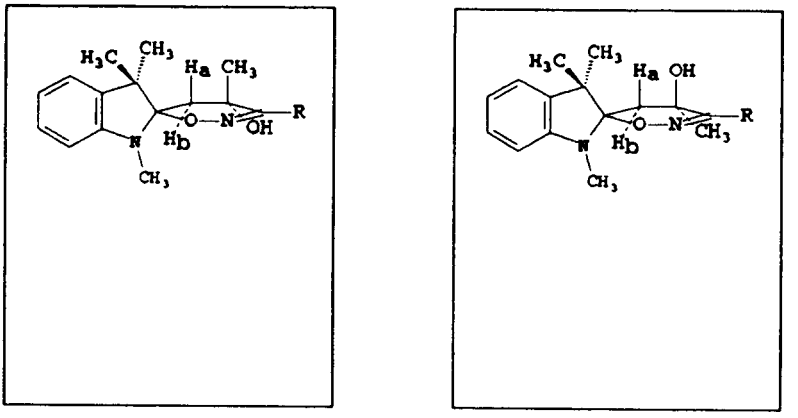


Fig. 4. Structural arrangement of diastereoisomers **I** (2R, 12S) and **II** (2R, 12R) of compound **7b**.

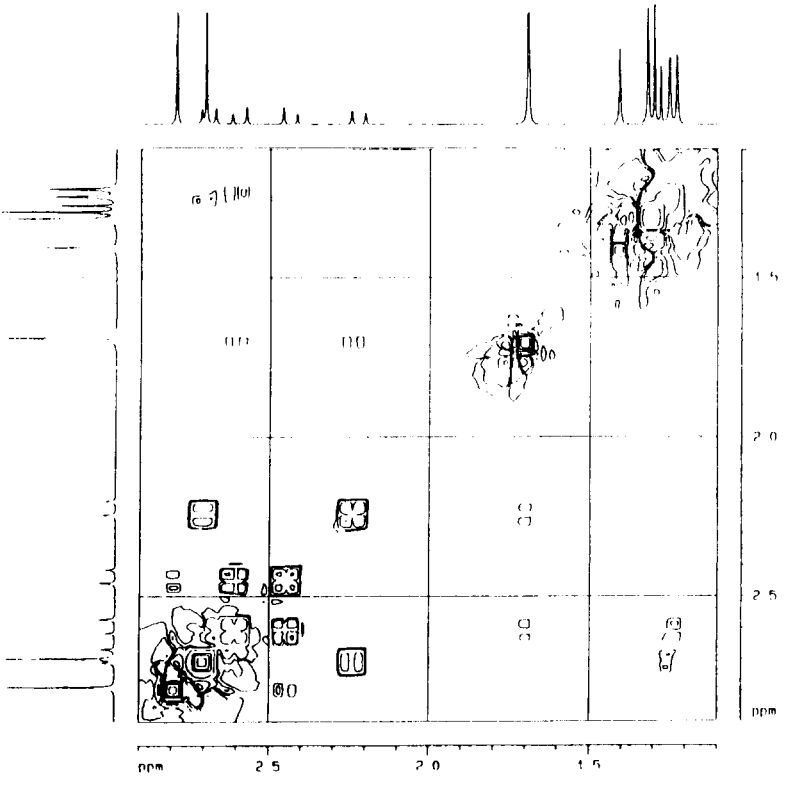
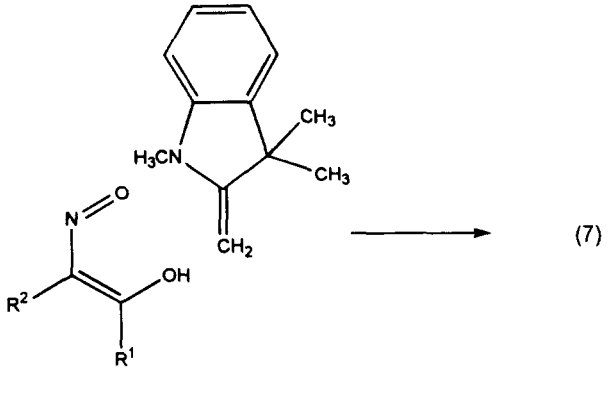


Fig. 5. Part of the NOESY spectrum of compound **7b** in deuteriochloroform. The spectrum was symmetrised.

data, for example the characteristic splitting pattern of the methylene group in the ^1H NMR spectra, were obtained for compounds **7b** and **7c**. The relative intensities of the signals due to the diastereoisomers of these compounds also showed time-dependence.

In compounds **7a–7c**, because of the presence of the two chiral carbon atoms (C-2 and C-12), the protons of the prochiral $C(11)H_2$ group and the protons and carbons of the methyl groups in the C(3) $(CH_3)_2$ arrangement are non-equivalent. The NOESY technique[13] is capable of detecting the space proximity of protons and has been used in this case to assign the signals to the two isomers (**I**), (2*R*, 12*S*) and (**II**), (2*R*, 12*R*) of compound **7b**. Figure 4 shows the arrangement of substituents in the isomers of compound **7b** and the NOESY spectrum of this compound is given in Fig. 5. The spectrum shows the proximity in space of proton H_a (resonating at 2.60 ppm) of the CH_2 group in isomer **I** with one of the (C-3)-methyl groups as well as with the (C-12)-methyl group. Proton H_b (δ = 2.45) in isomer **I** correlates with the N–CH_3 group (δ = 2.80). In contrast, proton H_a in isomer **II** (δ = 2.70) correlates only with one of the (C-3)-methyl groups (δ = 1.26), while a NOESY cross-peak between proton H_b (δ = 2.23) and the (C-12)-methyl group (δ = 1.703) confirms the proximity of these groups. A cross-peak due to the correlation of H_b with the N–CH_3 group (δ = 2.71) in isomer **II** coincides with that corresponding to the H_a/H_b interaction. Similar conclusions may be drawn for compounds **7a** and **7c**.

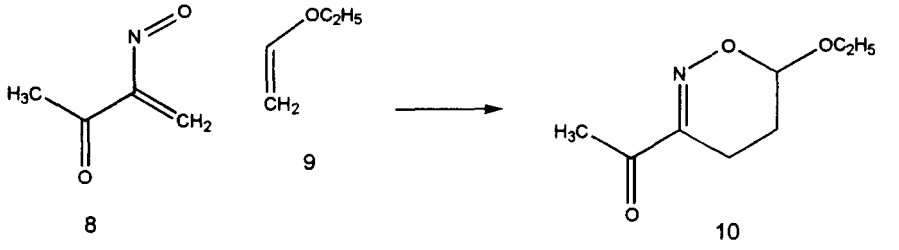
It seems likely that compounds **7a–7c** are formed by a Diels–Alder cycloaddition mechanism involving the reaction of the nitrosoenol tautomeric forms Y and Z of the isonitroso compounds (**4**) with Fischer's base, as is illustrated in Scheme 1.



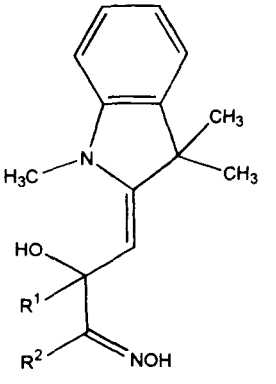
Scheme 1.

Reactions of nitrosoalkenes with electron-rich alkenes have been reported previously to give 1,2-oxazines.[15,16] For example, nitrosoalkene (**8**), generated as

a reactive intermediate, reacts with ethyl vinyl ether (**9**) to give the 1,2-oxazine (**10**).[16]



These reactions are examples of a Diels–Alder process with 'inverse electron demand', i.e. the heterodiene is the electron-deficient species and Fischer's base reacts as an electron-rich alkene. In such reactions a concerted one-step mechanism is preferred to a two-step process involving a dipolar intermediate.[16] Although Diels–Alder reactions are generally stereospecific, the formation of the two diastereoisomers might be expected in this case because of the possibility of geometrical isomerism (isomers Y and Z) of the nitrosoenol tautomers. In addition, the NMR evidence demonstrates that the diastereoisomers slowly interconvert. This interconversion may be due to the reversibility of the Diels-Alder process or alternatively it may proceed via a ring-opened species (**11**).



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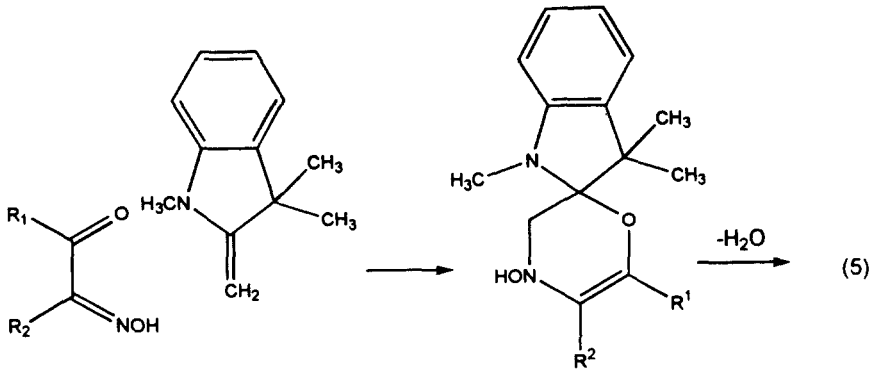
It seems likely that the mechanism of the formation of spiro-1,4-oxazines, such as compound **1**, involves an analogous heterocyclic Diels–Alder reaction of the ketooxime tautomer (X) with Fischer's base, followed by spontaneous dehydration of the cyclised product as shown in Scheme 2.



Scheme 2.

Compounds **7a–c** do not show any tendency to undergo the spontaneous dehydration which is observed in spiro-1,4-oxazine formation.

CONCLUSION

PPP MO calculations suggest that the merocyanine forms (**6**) of the hypothetical spiro-1,4-oxazines (**5**) might be expected to be high intensity red compounds. Attempted synthesis, however, led instead to dihydrohydroxyspiro-1,2-oxazines (**7**). These compounds do not exhibit photochromism.

EXPERIMENTAL

Instrumental methods

NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and X32 computer using the UXNMR software (Version 940501.3) for solutions in deuteriochloroform (**7b** and **7c**) or hexadeuteriodimethyl sulfoxide (**7c**). One-dimensional ^{1}H NMR (360.13 MHz) and ^{13}C NMR (90.566 MHz) spectra were recorded with 64 K data points and a spectral width of 5434.8 and 22727.2 Hz, respectively. ^{1}H and ^{13}C chemical shifts were referred to internal TMS (δ = 0.0) in $CDCl_3$, and to the central signal of solvent (δ = 2.55) (^{1}H) and 39.60 (^{13}C) in DMSO-D_6.

Experimental conditions for the measurement of two-dimensional NMR spectra[14] are reported for compound **7a**. Compounds **7b** and **7c** were measured analogously retaining approximately the digital resolutions.

H,H-COSY: d_1-90°-d_0-90°-Acq. Spectral width in both dimensions 2556.9 Hz, d_1 = 2 s, 1 K data points in F_2, 256 experiments in F_1, 4 dummy scans, 8 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, with zero-filling giving a matrix of 1 K x 1 K points.

NOESY: d_1-90°-d_0-90°-t_m-Acq. Spectral width in both dimensions 2556.9 Hz, d_1 = 5 s, t_m = 1.0 s, 1 K data points in F_2, 512 experiments in F_1, 4 dummy scans, 32 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, phase-sensitive processing with zero-filling giving a matrix of 1 K x 1 K points.

H,C-COSY: d_1-90°(^{1}H)-d_0-180°(^{13}C)-d_0-d_2-[90°(^{1}H)/90°(^{13}C)]-d_3-[decoupling/Acq]. Spectral width 13 513.5 Hz in F_2 and 2556.9 Hz in F_1, d_1 = 2 s, d_2 = 3.3 ms, d_3 = 2.2 ms. 1 K data points in F_2, 256 experiments in F_1, 4 dummy scans, 32 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, processing with zero-filling giving a matrix of 1 K x 512 points.

H,C-COSYLR: d_1-90°(^{1}H)-d_0-180°(^{13}C)-d_0-d_2-[90°(^{1}H)/90°(^{13}C)]-d_3- [decoupling/Acq]. Spectral width 13 513. 5 Hz in F_2 and 2 556.9 Hz in F_1, d_1 = 2 s, d_2 = 60 ms, d_3 = 40 ms. 1 K data points in F_2, 256 experiments in F_1, 4 dummy scans, 128 scans. Apodization with a $\pi/2$-shifted squared sine-bell function in both dimensions, processing with zero-filling giving a matrix of 1 K x 512 points.

1D INADEQUATE: d_1-90°(^{13}C)-d_2-180°(^{13}C)-d_2-90°(^{13}C)-d_3-90°(^{13}C)-[decoupling/Acq]. Spectral width 13 513.5 Hz, d_1 = 5 s, d_2 = 6.25 ms, d_3 = 3 μs, 64 K data points, 4 dummy scans, 10 240 scans.

The one-dimensional ^{15}N NMR (36.50 MHz) spectrum of compound **7a** (250 mg + 20 mg $Cr(acac)_3$ as relaxation reagent) was recorded in a 5 mm tube with 64 K data points and a spectral width of 18 250 Hz, d_1 = 4 s, 10 240 scans, inverse gated decoupling. ^{15}N chemical shifts were referred to external ^{15}N-enriched nitromethane (δ_N = 0.0) placed in a coaxial capillary.

Positive values of chemical shifts denote downfield shifts with respect to standards.

Melting points are peak temperatures determined using a Mettler DSC12E differential scanning calorimeter. Infrared spectra were recorded as KBr discs with a Perkin–Elmer 1740 Fourier Transform spectrometer. C, H and N analyses were carried out in the Department of Applied Chemical Sciences, Napier University, Edinburgh. Mass spectra were recorded using a Kratos MS9 double-focussing, forward geometry mass spectrometer.

PPP-MO calculations

A standard PPP-MO procedure was used within the fixed β approximation. A previously reported set of parameters was used.[6] Two-centre repulsion

integrals were determined using the Nishimoto–Mataga relationship[17] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly-excited configurations obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals.

Reaction of isonitroso compounds (4a–4c) with 1,3,3-trimethyl-2-methyleneindoline (3)

Isonitrosoacetoacetanilide **4a** (4.12 g, 0.02 moles) was dissolved in methanol (30 cm^3). To this solution was added 1,3,3-trimethyl-2-methyleneindoline (2.98 g, 0.02 moles) in methanol (15 ml). The mixture was stirred at room temperature in darkness for 24 h. The solution was reduced to dryness by rotary evaporation. The resulting material was crystallised from methanol to give compound **7a** (4.76 g, 63%) as yellow crystals (from methanol). m.p. 200°C (with exothermic decomposition). Found C, 69.7; H, 6.6; N, 10.9%; $C_{22}H_{25}N_3O_3$ requires C, 69.4; H, 6.6: N, 11.1%. ν_{max} 3497 (O–H), 3176 (N–H), 2 900–3050 (C–H), 1671 (C=O), 1607, 1597 (aromatic C–C), 1557, 1553 (amide II, N–H def.), 1534, 1488, 1445, 755, 741 (C–H def.) cm^{-1}; *m/z* 379 (2.1%) (M^+), 173 (16.0%), 158 (28.5%), 77 (10.6%), 49 (100%).

Compound **7b** (0.70 g, 11%) was obtained in a similar way from ethyl isonitrosoacetoacetate (**4b**) (3.18 g, 0.02 moles), using ethanol as reaction solvent, pale yellow crystals (from ethanol). m.p. 124°C (with exothermic decompostion). Found C, 74.3; H, 6.9; N, 8.7%; $C_{20}H_{22}N_2O_2$ requires C, 74.5; H, 6.9: N, 8.7%. ν_{max} 3343 (O–H), 2 800–3050 (C–H), 1714 (C=O); 1608 (aromatic C–C); 1562, 1489, 1457, 1432, 1411, 1366, 1310, 1197, 1151, 1100, 1062, 743 (C–H def.) cm^{-1}. *m/z* 332 (48.0%) (M^+), 314 (13.9%), 173 (52.8%), 172 (100%), 157 (82.4%).

Compound **7c** (0.60 g, 9%) was obtained in a similar way from isonitrosoacetophenone (**4c**) (2.98 g, 0.02 moles) as white crystals (from methanol) which tended to acquire a pink colour on drying. m.p. 120°C (with exothermic decomposition). Found C, 65.0; H, 7.3; N, 8.5%; $C_{18}H_{24}N_2O_4$ requires C, 65.0; H, 7.3: N, 8.4%. ν_{max} 3 086 (O–H), 2815–3060 (C–H), 1608, 1575 (aromatic C–C), 1489, 740, 704 (C–H def.) cm^{-1}; m/z 322 (28.8%) (M^+), 305 (21.1%), 174 (93.1%), 173 (98.4%), 158 (100%).

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