The Mechanism for Interconversion of Stereoisomers in *N*-(2,3-Dihydro-2-oxobenzoxazol-3-yl)- and *N*-(1,2-Dihydro-2-oxoquinolin-1-yl)-*N*-1-methylallylarenesulphenamides

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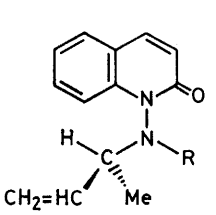
Stereoisomers of the quinolone and benzoxazolinone-substituted sulphenamides (1) and (2) are interconverted by formal rotation around their N–N (chiral) axes. Two alternative pathways which could result in net rotation have been tested. Neither epimerisation at C-1 *via* a route involving [2,3] sigmatropic rearrangement nor radical dissociation–recombination have been found to contribute significantly to interconversion of the stereoisomers. The retarded rate of steroisomer interconversion in the 4-methylbenzoxazolinone-sulphenamide (16) by comparison with (2) suggests that this process in (2) occurs by simple N–N bond rotation and a similar conclusion has been drawn in the case of (1) by comparison with the rate of racemisation of (19).

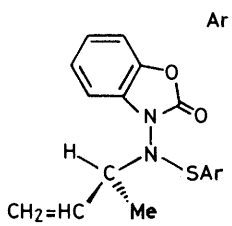
The quinolone-substituted sulphenamide (1) has been separated into two crystalline stereoisomers [1,2] which slowly interconvert in solution over 1 h at 80 °C. From a study of analogues of (1), it was concluded that the additional chirality which gave rise to these stereoisomers was an N–N chiral axis, the result of restricted rotation around the N–N bond.[3]

By contrast, the benzoxazolinone-substituted sulphenamide [1] (2) shows a broadened singlet for the methyl group (δ 1.41) which separates into two doublets [δ 1.36 and 1.50 (J 6.5 Hz) ratio 2 : 3] as the temperature is lowered and collapses to a doublet at higher temperature ($\Delta G^{\ddagger}$ *ca.* 15.5 kcal mol^{-1}). N–N Bond rotation in (2), therefore, appears to be considerably facilitated by comparison with (1).

In this paper we examine the process by which apparent N–N bond rotation in (1) and (2) actually occurs. Thus, in addition to a simple rotation, there exist at least two other pathways deserving of consideration by which formal N–N bond rotation could be accomplished. The first of these is illustrated in Scheme 1 using the quinolone-substituted sulphenamide (1) as an example and includes the reverse of the reaction by which (1) was formed, namely [2,3] sigmatropic rearrangement to the sulphilimine (5).[1]



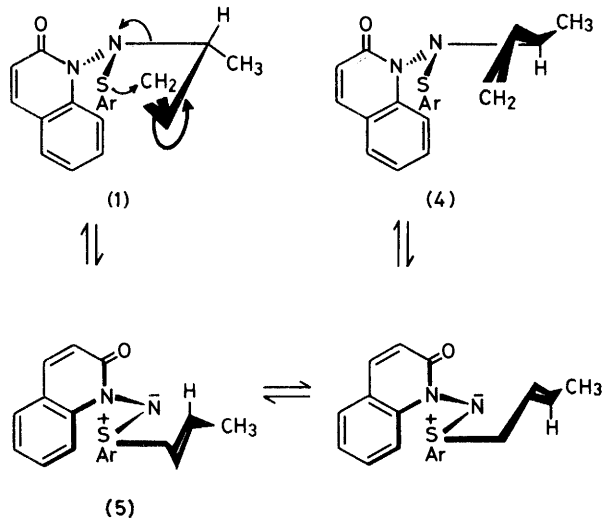
(1) R = SAr
(3) R = H



(2)

Following the pathway shown in Scheme 1, the overall conversion (1) ⟶ (4) is an inversion of configuration at C-1 in the sulphenamide (1) without the necessity for N–N bond rotation [though the latter process might well be easier within the sulphilimine (5) than the sulphenamides (1) and (4)]. A change in the configuration at C-1 is, in a racemic substrate, equivalent to a rotation around the N–N bond.

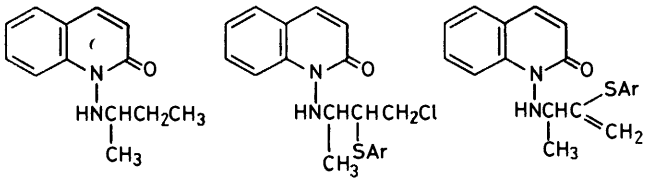
In principle, the intervention of this route for interconversion of the stereoisomers can easily be tested by removal of the double bond which would eliminate the possibility of the [2,3] sigmatropic rearrangement (1) ⟶ (5). In practice, the method for making (1) does not lend itself to synthesis of saturated analogues and removal of the double bond in (1) without cleavage of the labile N–S bond proved difficult. Thiolysis of (1) gave the amine (3) which was hydrogenated to (6). Attempts to re-sulphenylate (6) with *p*-chlorosulphenyl chloride were unsuccessful.



Scheme 1

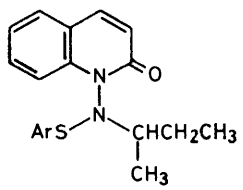
An attempt to add *p*-chlorosulphenyl chloride to the double bond of (1) also resulted in N–S bond cleavage giving a crystalline product (7) of unknown stereochemistry. Dehydrohalogenation of (7) using sodium hydride in dimethylformamide gave the crystalline vinyl sulphide (8) whose structure followed unambiguously from n.m.r. and supported the orientation of the *p*-chlorosulphenyl chloride addition as in (7).

Eventually it was found that the double bond in (1) could be reduced and the N–S bond retained using a new method of generating di-imide from hydrazine and *N*-chlorodi-isopropylamine.[4] This method was applied to a 1 : 1 mixture of the two stereoisomers of (1) and also to



(6) (7) (8)

a 5 : 1 mixture with the stereoisomer having the methyl doublet in the n.m.r. at δ 0.93 in excess. Comparison of the products after removal of a little amine (6) by chromatography over Kieselgel revealed considerable differences, and as a result, equilibration between the two reduced stereoisomers (9) initially present in a 5 : 1 ratio could be followed. In particular, a doublet (due to a 1-methyl group) at δ 1.30 was diminished in intensity as a second doublet at δ 1.90 increased on heating in chlorobenzene at 82 °C. Accurate kinetic measurements of the rate of equilibration were difficult to make because of overlap of peaks but the time taken for equilibration (no further change in the n.m.r. spectrum) was not measurably different from that for (1) ⇌ (4)] at the same temperature and stereoisomer starting ratio.

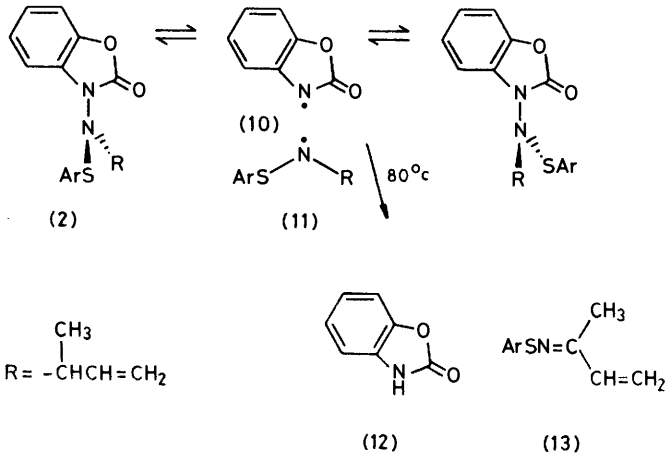


(9)

The alternative route for N–N bond rotation in Scheme 1 seems, therefore, to be excluded for (1) and probably also for (2) since it seems unlikely that the nature of the heterocycle would have much effect upon the rate of the individual steps involved in Scheme 1.

A second alternative route to formal N–N bond rotation involves homolysis of the N–N bond with recombination after rotation of one of the radicals illustrated for the benzoxazolinone-substituted sulphenamide (2) in Scheme 2.

This possibility must be seriously considered since we have shown [5] that the two radicals (10) and (11) can be identified by e.s.r. spectroscopy in thermally decomposing solutions of (2) at 105 °C in chlorobenzene. Whereas (2) decomposes to benzoxazolinone (12) and the thio-oxime (13) within 2 h in boiling benzene, (1) is only 13% decomposed on heating to 100 °C for 2 h although it gives the same thio-oxime (13) and quinolin-2-one and presumably decomposes *via* the same radical pathway as in Scheme 2. Homolysis–recombination (without decomposition) at lower temperatures would seem a real possibility, therefore, for permitting N–N bond rotation.



(2) (10) (11) (12) (13)

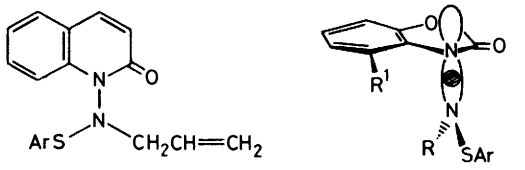
SCHEME 2

Attempts to test for the importance of this route by cross-over experiments between (excess) (2) and (14) on heating in chlorobenzene were negative.

A more bulky substituent R^1 than H at position 4 of the benzoxazolinone ring would increase the barrier to simple rotation whereas the effect of such a substituent on the rate of homolysis would almost certainly be to increase the latter. This is particularly so if, as we believe, homolysis of (2) takes place *via* the conformation indicated in (15; R^1 = H) where the developing unpaired electron can be resonance delocalised over the π-systems of the aromatic ring and carbonyl group.

To minimise any interaction other than a steric one we elected to synthesise the 4-methyl-substituted analogue of (2), *i.e.* (16) which was accomplished as shown in Scheme 3.

Amination of 4-methylbenzoxazolinone (17) using hydroxylamine *O*-sulphonic acid proceeded in poor

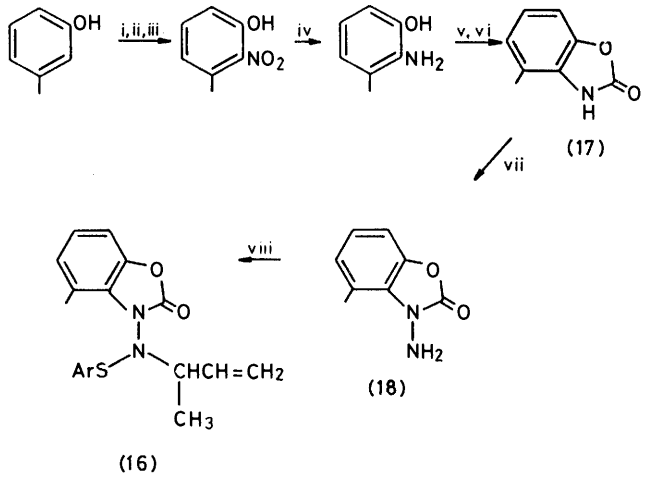


(14) (15)

yield (10%): the major product was unchanged starting material but the *N*-amino-compound (18) was conveniently separated from (17) by taking advantage of the solubility of the latter in base.

Oxidation of 3-amino-4-methylbenzoxazolinone (18) with lead tetra-acetate in the presence of *p*-chlorophenyl crotyl sulphide followed by rapid chromatography over alumina gave the sulphenamide (16) as an oil whose n.m.r. spectrum was particularly informative. Initially, two doublets were present at δ 1.18 and 1.50

(both J 6-Hz, ratio *ca.* 3 : 1) which can be assigned to the 1-methyl groups in the two stereoisomers. Monitoring this n.m.r. solution over several hours showed clearly that slow interconversion between the two stereoisomers was taking place; after 11 h at room temperature the ratio δ 1.18 : 1.50 was *ca.* 1 : 1. A similar change in ratio was evident in the aromatic ring methyl group signals of both stereoisomers at δ 2.20 and 2.16.



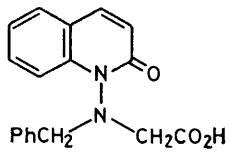
SCHEME 3 Reagents: i, H_2SO_4; ii, HNO_3; iii, H_2O; iv, H_2–Pd; v, $ClCO_2Et$–pyridine; vi, heat; vii, NH_2OSO_3H; viii; $Pb(OAc)_4$–$ArSCH_2CH{=}CHCH_3$

Interconversion of the stereoisomers is not the only change taking place during the 11 h at room temperature: the onset of decomposition into thio-oxime (13) and 4-methylbenzoxazolinone (17) is underway as indicated by the appearance of their respective methyl signals at δ 2.08 and 2.34. After 5 days at room temperature, decomposition into thio-oxime (13) and 4-methylbenzoxazolinone (17) was complete and pure (17) crystallised in the n.m.r. sample tube.

From this n.m.r. behaviour and bearing in mind that interconversion of stereoisomers in the case of (2) is becoming fast on the n.m.r. time-scale at room temperature, it can be concluded that homolysis–recombination, or even heterolysis–recombination,* does not contribute significantly towards this interconversion in (2) since introduction of the 4-methyl substituent has drastically increased the barrier.

As predicted, the rate of decomposition of (16) into thio-oxime (13) and benzoxazolinone (17) has increased by comparison with the analogous decomposition of (2). Interconversion of stereoisomers in the case of (16) is well underway before observable decomposition into (13) and (17).

For the case of the quinolinone-substituted sulphenamide (1), we have not measured rates of stereoisomer interconversion in the 8-methyl-substituted analogue. However, in (1) also, radical homolysis–recombination is unlikely as a route. Thus the glycine derivative (19) has

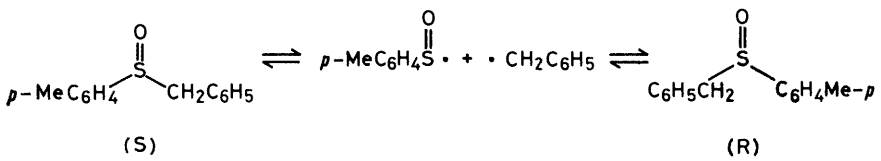


(19)

been resolved [6] and the barrier to racemisation measured. The value obtained for $\Delta G^{\ddagger}$ (corresponding to rotation around the N–N chiral axis) is 26.2 ± 0.4 kcal mol^{-1} and is in good agreement with the barrier separating the stereoisomers in (1) (26.1 kcal mol^{-1}) [homolysis–recombination can be discounted as a route for the racemisation of (19)].

Evidence against the homolysis–recombination mechanism in (1) comes also from the magnitude of the calculated entropy of activation $\Delta S^{\ddagger}$ of 0.9 ± 2 cal mol^{-1} K^{-1} for the interconversion of its stereoisomers. This contrasts with a value of +25 cal mol^{-1} K^{-1} for the racemisation of benzyl *p*-tolyl sulphoxide which is believed to proceed *via* benzyl and arylsulphinyl radicals [7] (Scheme 4).

It is perhaps surprising that the two barriers to rotation in (19) and (1) should be so similar even if both do correspond to N–N bond rotation. When rotation around the N–N bond takes place, the barrier corresponds to the steric (and electronic) interaction between two pairs of substituents together with N,N lone pair–lone pair repulsion. Two barriers (20) and (21) can be envisaged and the smaller of the two will be that measured. The similarity of the two barriers for (19) and (1) can be rationalised by assuming that the *peri*-H-8–$CH_2Ph(CH_2CO_2H)$ interaction is similar to the *peri*-H-8–$CH(CH_3)CH{=}CH_2$ interaction and both these contribute significantly more to the rotational barrier than any interaction of substituents with the quinolinone C=O.†

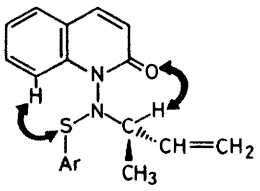


SCHEME 4

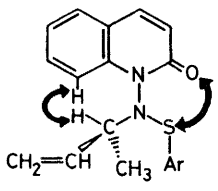
* Heterolysis–recombination in the case of (1) (quinolone anion) can be excluded since $\Delta G^{\ddagger}$ for (1) (26.1 kcal mol^{-1}) is similar to or even greater than that of its *p*-nitrophenylthio analogue (25.3 kcal mol^{-1}) (see ref. 3).

† It is possible that the magnitude of the SAr group interaction with *peri*-H-8 is similar to that of $CH(CH_3)CH{=}CH_2$ but it cannot be smaller.

A similarly diminished barrier to rotation in benzoxazolinone by comparison with quinolone-substituted derivatives is observable in (22) in which the diastereotopic protons within each benzyl group appear as an

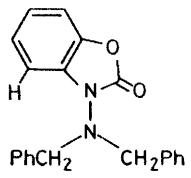


(20)



(21)

AB system and undergo coalescence at 95 °C ($\Delta G^{\ddagger}$ 18.4 kcal mol^{-1}) whereas, as expected by comparison with (19), the corresponding benzyl protons in (23) remain identifiable as an AB system up to 180 °C in nitrobenzene solution by n.m.r.



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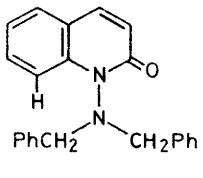

(23)

The facility of N–N bond rotation in benzoxazolone derivatives (2) and (22) by comparison with quinolone analogues (1) and (23) respectively can be attributed to the change in heterocyclic ring size from six to five which alleviates the *peri*-H–>CH interaction.

EXPERIMENTAL

For general experimental procedures and details of instrumentation, see ref. 3.

1-(1-*Methylallylamino*)*quinolin*-2(1H)-*one* (3).—A solution of sodium 4-chlorobenzenethiolate was prepared by dissolving sodium (0.3 g) in ethanol (50 ml) and adding 4-chlorobenzenethiol (1.4 g). To this solution was added *N*-(1,2-dihydro-2-oxoquinolin-1-yl)-*N*-(1-methylallyl)-4-chlorobenzenesulphenamide (1) (2.2 g) and the mixture heated under reflux for 1.5 h. Ethanol was removed under reduced pressure and the residue partitioned between chloroform (50 ml) and sodium hydroxide solution (1M; 30 ml). The chloroform layer was washed with water, dried, and evaporated and the oily residue chromatographed over basic alumina (90 g). Elution with light petroleum–ethyl acetate (9 : 1) gave bis-(4-chlorophenyl) disulphide (1.24 g) and further elution with ethyl acetate gave the *product* (3) (1 g, 76%) as crystals (from light petroleum), m.p. 80.5—81 °C (Found: C, 73.0; H, 6.6; N, 13.0. $C_{13}H_{14}N_2O$ requires C, 72.9; H, 6.6; N, 13.1%); δ($CDCl_3$) 7.61 (d, *J* 9.5 Hz, quinoline H-4), 7.96—6.98 (m, 4 ArH), 6.67 (d, *J* 9.5 Hz, quinoline H-3), 6.51br (s, exch. D_2O, NH), 6.0—5.6 (m, =CH–), 5.0—4.7 (m, $=CH_2$), 4.08—3.64 (m, NC*H*), and 1.23 (d, *J* 7 Hz, CH_3); $\nu_{max.}$ 3 240m, 1 650s, 1 590s, 1 005w, 930s, 830s, and 760s cm^{-1}; *m/e* 214 (M^+), 199, 160, 159, 146, 145 (base), 131, 117, 103, 89, and 55.

1-(1-*Methylpropylamino*)*quinolin*-2(1H)-*one* (6).—The foregoing alkene (1 g) was hydrogenated at atmospheric pressure in ethanol (25 ml) in the presence of 10% palladium on charcoal (0.4 g) until the uptake of hydrogen ceased. After separation of the catalyst and evaporation of the solvent, the residue was passed through a short column of basic alumina (10 g) with ethyl acetate which gave the *product* (6) (0.74 g, 73%) as crystals (from light petroleum), m.p. 63—65 °C (Found: C, 72.05; H, 7.4; N, 12.75. $C_{13}H_{16}N_2O$ requires C, 72.2; H, 7.5; N, 12.95%); δ($CDCl_3$) 8.00 (d, *J* 9 Hz, quinoline H-8), 7.75 (d, *J* 9.5 Hz, quinoline H-4), 7.7—7.1 (m, 3 ArH), 6.75 (d, *J* 9.5 Hz, quinoline H-3), 5.7br (s, exch. D_2O, NH), 3.35 (m, NCH), and 1.8—0.8 (m, 8 aliphatic H); $\nu_{max.}$ 3 280s, 1 655s, 1 595s, 1 410m, 1 230m, 1 145m, 830s, 750s, and 740m cm^{-1}.

Reaction of (1) *with* 4-*Chlorobenzenesulphenyl Chloride*.—The sulphenamide (1) (2 g) was set aside with *p*-chlorobenzenesulphenyl chloride (3 g) in chloroform (20 ml) overnight. After removal of the solvent, the residue was chromatographed over alumina. Light petroleum–ethyl acetate (9 : 1) eluted an unidentified faster running fraction and further elution with ethyl acetate gave, after crystallisation from ethanol, 1-[3-*chloro*-2-(4-*chlorophenylthio*)-1-*methylpropylamino*]*quinolin*-2(1H)-*one* (7) (0.7 g) as crystals, m.p. 139—139.5 °C (Found: C, 58.1; H, 4.5; N, 7.2. $C_{19}H_{18}Cl_2N_2OS$ requires C, 58.0; H, 4.6; N, 7.1%); δ($CDCl_3$) 8.2—7.2 (m, 8 ArH + quinoline H-4), 6.92 (d, *J* 9.5 Hz, quinoline H-3), 6.45br (s, exch. D_2O, NH), 4.2—3.6 (m, 4 aliphatic H), and 1.32 (d, *J* 7 Hz, CH_3); $\nu_{max.}$ 3 265w, 1 645s, 1 585s, 1 090m, 1 005m, 815s, and 750s cm^{-1}; *m/e* 396/394/392 (M^+), 358/356, 233/231, 213, 187, 149, and 145.

1-[2-(4-*Chlorophenylthio*)-1-*methylallylamino*]*quinolin*-2(1H)-*one* (8).—The foregoing product (7) (123 mg) was stirred in freshly distilled dimethylformamide (1.5 ml) with sodium hydride (50% dispersion; 20 mg). After 1 h at room temperature the mixture was poured into water (5 ml) and the gum obtained triturated giving a solid which was crystallised from ethanol to yield the *sulphide* (8) (70 mg, 63%), m.p. 119.5—121 °C (Found: C, 63.9; H, 4.8; N, 7.8. $C_{19}H_{17}ClN_2OS$ requires C, 63.95; H, 4.8; N, 7.85%); δ($CDCl_3$) 8.0 (d, *J* 8 Hz, quinoline H-8), 7.7—7.0 (m, 7 ArH + quinoline H-4), 6.60 (d, *J* 9.5 Hz, quinoline H-3), 5.75br (d, *J* 4 Hz, exch. D_2O, NH), 5.3br (s, =CH *cis* to S), 4.7br (s, =CH *trans* to S), 4.0 (m, NCH; becomes q, *J* 6.5 Hz after exch. D_2O), and 1.28 (d, *J* 6.5 Hz, CH_3); $\nu_{max.}$ 3 230w, 1 660s, 1 590s, 1 090m, 1 010m, 860m, 830s, and 760s cm^{-1}.

N-(1,2-*Dihydro*-2-*oxoquinolin*-1-*yl*)-N-(1-*methylpropyl*)-4-*chlorobenzenesulphenamide* (9).—The sulphenamide diastereoisomer of (1) having δ(CCl_4) 0.93 (Me) (0.12 g) and hydrazine hydrate (0.9 g) were dissolved in methanol (7 ml) at 0 °C and a solution of *N*-chlorodi-isopropylamine (2.44 g) in methanol (4 ml) added slowly with stirring. After 1.5 h at 0 °C, the methanol was removed and dichloromethane (10 ml) and water (10 ml) added. The organic layer was washed with water, dried, and evaporated. Since n.m.r. indicated only partial conversion to the required product, the residue was redissolved in methanol (8 ml) and hydrazine hydrate (1 g) added and the mixture cooled to 0 °C. *N*-Chlorodi-isopropylamine (2.7 g) in methanol (5 ml) was added slowly. Working-up as described above gave an oil whose n.m.r. spectrum showed the absence of olefinic protons. Chromatography over Kieselgel (5 g) eluting with dichloromethane gave bis-(4-chlorophenyl) disulphide (15 mg) followed by the *sulphenamide* (9) (52 mg, 43%) as a glass. (Found: *m/e*, 301.020 5. $C_{15}H_{10}ClN_2OS$ requires

M, 301.020 2. Found: *m/e*, 213.037 5. $C_{10}H_{12}ClNS$ requires *M*, 213.037 7); δ($CDCl_3$) 8.0—7.0 (m, 8 ArH + quinoline H-4), 6.70 (d, *J* 9.5 Hz, quinoline H-3), 4.10 (m, NCH), and 2.2—0.8 (m, 5 aliphatic H including d, *J* 7 Hz at δ 1.30, CH_3); *m/e* 360/358 (M^+), 303/301, 215/213, 188/186, 145 (base), 117, and 108.

Further elution with dichloromethane gave (6) (25 mg, 34%) identical with a sample prepared as described above.

N-Allyl-N-(1,2-dihydro-2-oxoquinolin-1-yl)-4-chlorobenzenesulphenamide (14).—Prepared from 1-aminoquinolin-2(1*H*)-one and allyl 4-chlorophenyl sulphide by the method previously described [1] as *crystals* (49%) (from light petroleum), m.p. 83.5—85° (Found: C, 63.1; H, 4.5; N, 8.2. $C_{18}H_{15}ClN_2OS$ requires C, 63.1; H, 4.4; N, 8.2%), δ($CDCl_3$) 7.9—7.2 (m, 8 ArH + quinolone H-4), 6.7 (d, *J* 9.5 Hz, quinolone H-3), 6.4—5.0 (m, 3 olefinic H), and 4.5br (d, *J* 6.5 Hz, NCH_2); $\nu_{max.}$ 1 650s, 1 595s, 1 240m, 1 010w, and 830s cm^{-1}.

Attempted Cross-over Experiment between (2) *and* (14).—The sulphenamides (2) (293 mg, 0.85 mmol) and (14) (116 mg, 0.34 mmol) were dissolved in benzene and heated under reflux for 2 h. Evaporation of benzene and chromatography over alumina gave the sulphenylimine (13) (120 mg, 67%) as a yellow oil eluted with light petroleum. Elution with light petroleum–ethyl acetate (1 : 1) gave unchanged (14) (101 mg) in which no (1) was detectable by n.m.r.

4-Methylbenzoxazole-2(3H)-one (17).—2-Nitro-*m*-cresol was prepared by the method of Hodgson and Beard [8] and purified *via* its crystalline acetate using Gibson's procedure.[9] 3-Methyl-2-aminophenol was obtained by catalytic reduction of 2-nitro-*m*-cresol in ethanol using 10% palladium on charcoal and hydrogen. Reaction of equimolar quantities of 3-methyl-2-aminophenol and ethyl chloroformate in dry pyridine and heating the isolated crude product at 220 °C for 10 min gave (17) (71%), m.p. 156—158 °C (from ethanol) (lit.,[10] 158—159 °C).

3-Amino-4-methylbenzoxazol-2(3H)-one (18).—The benzoxazolone (17) (1 g) and potassium carbonate (2.8 g) were dissolved in water (17 ml) containing ethanol (3.5 ml). This solution was heated to 65 °C and hydroxylamine *O*-sulphonic acid (1 g) added over 5 min keeping the temperature at 60—65 °C. Water (50 ml) was then added and the solid separated off. This solid was extracted between sodium hydroxide solution (2M, 20 ml) and benzene (20 ml) and the organic layer separated, washed with water, dried, and evaporated. Crystallisation of the residual solid (110 mg, 10%) from chloroform–light petroleum gave the *product* (18) as needles, m.p. 155—156 °C (Found: C, 58.45; H, 4.85; N, 17.15. $C_8H_8N_2O_2$ requires C, 58.55; H, 4.9; N, 17.05%); δ($CDCl_3$) 6.90 (s, 3 ArH), 4.45br (s, NH_2), and 2.61 (s, CH_3); $\nu_{max.}$ 3 328m, 3 204w, 1 760s, and bands at 1 347m, 1 218m, 1 133s, and 1 004s cm^{-1} which were absent in (17).

Acidification of the separated basic solution above and crystallisation of the solid from ethanol–water gave the starting benzoxazolone (17) (0.6 g).

N-(2,3-Dihydro-4-methyl-2-oxobenzoxazol-3-yl)-N-(1-methylallyl)-4-chlorobenzenesulphenamide (16).—Powdered lead tetra-acetate (536 mg) was added over 5 min to an ice-cooled and magnetically stirred solution of the aminobenzoxazolone (18) (200 mg) and *trans*-but-2-enyl 4-chlorophenyl sulphide (450 mg) in dichloromethane (1.8 ml). After stirring for a further 15 min, lead diacetate was separated and the bulk of the dichloromethane removed under reduced pressure without warming. The residue was chromatographed directly and rapidly through a small column of alumina made up in benzene. After elution of residual crotyl sulphide, carbon tetrachloride eluted the sulphenamide (16) having δ(CCl_4) 7.51, 7.37, 7.28, 7.14 (4 lines of AA'BB' system, 4 × ArH), 7.0—6.7 (m, 3 benzoxazole H), 6.2—5.0 (m, $CH{=}CH_2$), 4.7—4.4 (m, $CHCH_3$), 2.20 and 2.16 (2 × s, 4-CH_3), and 1.50 and 1.18 (2 × d, 1'-CH_3). The initial ratio of δ 2.20 : 2.16 or 1.18 : 1.50 was 3 : 1 and changed on setting aside in CCl_4 solution to 1 : 1 over 11 h at ambient temperature. After 5 days at room temperature, the n.m.r. sample tube contained only 4-methylbenzoxazolone (17) and thio-oxime (13).

3-(Dibenzylamino)benzoxazol-2(3H)-one (22).—3-Aminobenzoxazolin-2(3*H*)-one (400 mg) and benzyl bromide (2 ml) were heated under reflux for 0.75 h under nitrogen. Excess of benzyl bromide was removed using an oil pump, the residue poured into concentrated ammonia solution (50%, 20 ml), and extracted with dichloromethane (2 × 15 ml). The organic extracts were dried and evaporated and the residue purified by chromatography over Kieselgel (25 g) eluting with light petroleum–ethyl acetate (2 : 1). After elution of residual benzyl bromide, the *product* was obtained (167 mg, 19%) as crystals (from ethanol), m.p. 112—114 °C (Found: C, 76.3; H, 5.55; N, 8.4. $C_{21}H_{18}N_2O_2$ requires C, 76.3; H, 5.5; N, 8.5%); δ($CDCl_3$) 7.5—7.0 and 6.8 (m, 14 ArH); and 4.40 (AB system, J_{AB} 12.5 Hz, 2 × CH_2Ph); $\nu_{max.}$ 1 750s, 1 250m, 1 120m, 1 010m, 990m, 750s, 700s, and 670s cm^{-1}.

1-(Dibenzylamino)quinolin-2(1H)-one (23).—Prepared as for (22) from 1-aminoquinolin-2(1*H*)-one (0.6 g) and benzyl bromide (4 ml) under reflux for 0.5 h. Chromatography as above gave the *product* (160 mg, 12%) as crystals (from light petroleum–chloroform), m.p. 81—82 °C (Found: C, 81.0; H, 6.0; N, 8.2. $C_{23}H_{20}N_2O$ requires C, 81.15; H, 5.9; N, 8.2%); δ($CDCl_3$) 8.0 (d, *J* 9 Hz, quinolone H-8), 7.54 (d, *J* 9.5 Hz, quinolone H-4), 7.4—6.9 (m, 13 ArH), 6.64 (d, *J* 9.5 Hz, quinolone H-3), and 4.58 (AB system, J_{AB} 12.5 Hz, 2 × CH_2Ph); $\nu_{max.}$ 1 655s, 1 600s, 990m, 830s, 750s, and 700s cm^{-1}.

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