

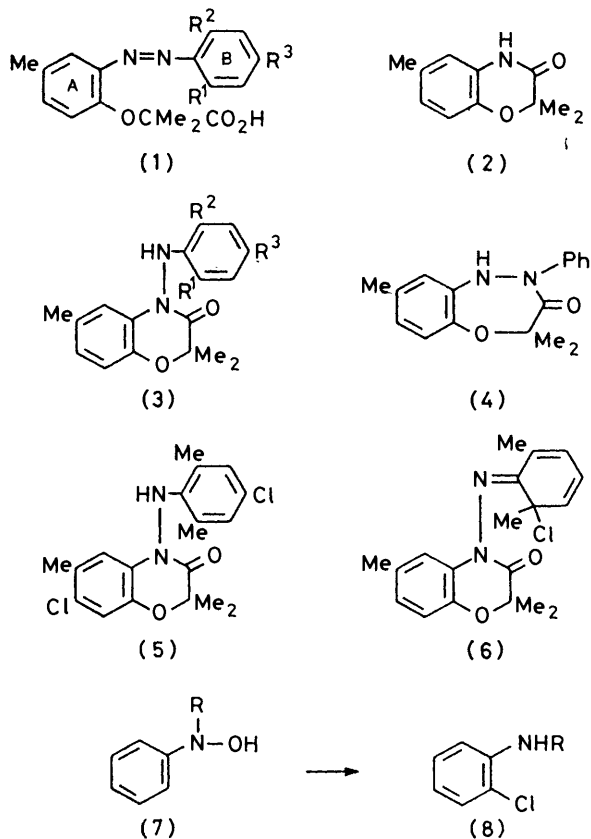
## A New Reaction of Acid Chlorides. Intramolecular *ortho*-Chlorination

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2-(2-Arylazophenoxy)-2-methylpropanoic acids (1) react with thionyl chloride to form 4-(2-chloroanilino)-benzoxazinones (3) in high yield. The reaction proceeds through the acid chloride which undergoes cyclisation with intramolecular electrophilic transfer of the chlorine to ring B. This selective *ortho*-chlorination is general for azo-acids (1) in which ring B contains a free *ortho*-position and  $-M$  groups are absent.

2-(2,6-Dimethylphenylazophenoxy)-2-methylpropanoic acid reacts to give the 4-(4-chloro-2,6-dimethylanilino)benzoxazinone but this *para*-chlorination (and a little dichlorination) is probably an intermolecular process.

THE product of the reaction of a carboxylic acid with thionyl chloride is not invariably the corresponding acid chloride.<sup>1</sup> We report another abnormal reaction with this reagent.



In connection with other work we treated the azo-acid (1;  $R^1 = R^2 = R^3 = H$ ) with an excess of boiling thionyl chloride in the usual way. The product,  $C_{17}H_{17}ClN_2O_2$ , obtained in 92% yield, was isomeric with the expected acid chloride and contained only seven aromatic protons (n.m.r.). On catalytic hydrogenation it gave the spectroscopically similar dechloro-compound,  $C_{17}H_{18}N_2O_2$ , and another product identified as the lactam (2).<sup>2</sup> As both of these compounds were also obtained by hydrogenation of the starting acid (1;  $R^1 = R^2 = R^3 = H$ ) the dechloro compound appeared to be the benzoxazinone (3;  $R^1 = R^2 = R^3 = H$ ), the

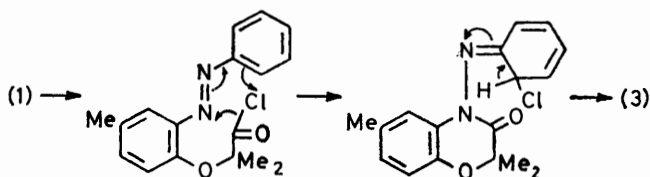
isomeric lactam (4) being excluded on account of its less favourable ring size, and the difficulty of converting (4) into (2) under our conditions. An important peak in the mass spectrum of the chloro compound at  $m/e$  190 ( $M^+ - C_8H_5ClN$ ) suggested that the chlorine atom was attached to the anilino group, and its position *ortho* to the nitrogen was established by spin decoupling of the europium-shifted n.m.r. spectrum. This was confirmed by an independent synthesis starting from the *o*-chloroazo-acid (1;  $R^1 = Cl$ ,  $R^2 = R^3 = H$ ). Reduction with diimine gave the hydrazo compound which spontaneously cyclised to the chlorobenzoxazinone (3;  $R^1 = Cl$ ,  $R^2 = R^3 = H$ ) identical with that obtained by reaction of the azo-acid (1;  $R^1 = R^2 = R^3 = H$ ) with thionyl chloride.

This selective *ortho*-chlorination appears to be a general reaction provided that ring B of the starting acid (1) contains a free *ortho* position and no  $-M$  substituents. This is strikingly demonstrated by the conversion of the azo-acid (1;  $R^1 = Cl$ ,  $R^2 = R^3 = H$ ) into the dichloro-anilino benzoxazinone (3;  $R^1 = R^2 = Cl$ ,  $R^3 = H$ ) in 92% yield. In all cases the position of the chlorine atoms was deduced from the europium-shifted n.m.r. spectra in which all the aromatic proton signals were clearly separated.

When the parent azo-acid (1;  $R^1 = R^2 = R^3 = H$ ) was allowed to react with thionyl chloride in the cold for 30 min, and then quenched with boiling methanol, the benzoxazinone (3;  $R^1 = Cl$ ,  $R^2 = R^3 = H$ ) was isolated in much lower yield (40%) together with the methyl ester of the acid. This shows that the first stage in the reaction is the formation of the normal acid chloride. The subsequent aromatic chlorination is an intramolecular process since (a) chlorine-free products were not detected (but see below), (b) when the reaction with the acid (1;  $R^1 = Cl$ ,  $R^2 = R^3 = H$ ) was carried out in the presence of anisole no products derived from anisole could be found, and (c) all attempts to effect an intermolecular reaction between azobenzene and acid chlorides (or acids and thionyl chloride) were unsuccessful. Our failure to effect this intermolecular reaction is in contrast with the rapid reaction<sup>3</sup> of *cis*-azobenzene with acetyl chloride in the dark to give mono- and di-*N*-acetyl-4-chlorohydrazobenzene. A similar result<sup>4</sup> was obtained with *trans*-azobenzene on photolysis or on exposure to sunlight (in Australia!), the first step being *trans*-*cis*

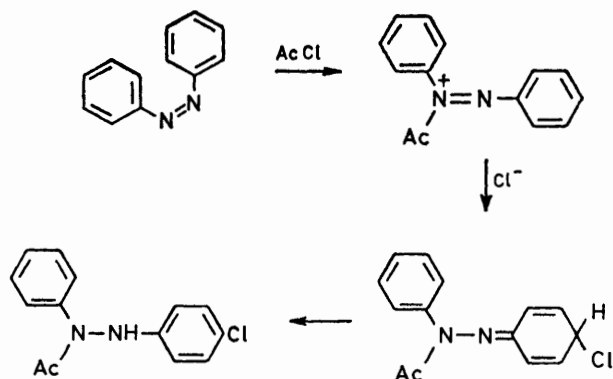
isomerisation of the azo-compound. We also failed to effect reaction between the azo-acid (1;  $R^1 = R^2 = R^3 = H$ ) and hydrogen chloride under our chlorination conditions which excludes the possibility that the reaction proceeds by way of addition of hydrogen chloride to the azo linkage<sup>5</sup> followed by cyclisation to the *N*-chloro derivatives of (3) and subsequent chlorine rearrangement; in any case that would be expected to lead to mainly *para*-substitution.

Thus we conclude that the reaction proceeds as shown in Scheme 1, the mechanism being strongly favoured by the formation in the transition state of two six-membered rings. That the chlorination is electrophilic, as shown,



SCHEME 1

is supported by quantitative measurements on the reactions with the 4'-methoxy-, 4'-nitro-, and the parent acid. When the acids were treated with an excess of thionyl chloride in carbon tetrachloride at 35 °C and the rate of disappearance of the azo-acids was measured by u.v. spectroscopy, the first-order rate constants for the 4-methoxy- and the parent acid were evaluated as  $1.19 \times 10^{-4}$  and  $9.16 \times 10^{-6} \text{ s}^{-1}$ , respectively. Under these conditions reaction of the 4'-nitro acid was immeasurably slow. Scheme 1 should be compared with the mechanism proposed<sup>3</sup> for the interaction of *cis*-azobenzene and acetyl chloride (Scheme 2) where the

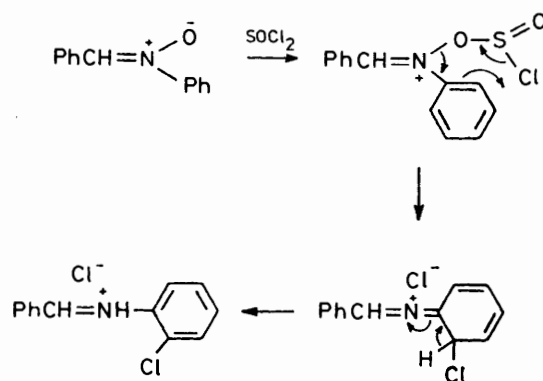


SCHEME 2

chlorination is nucleophilic and occurs in the *para*-position.

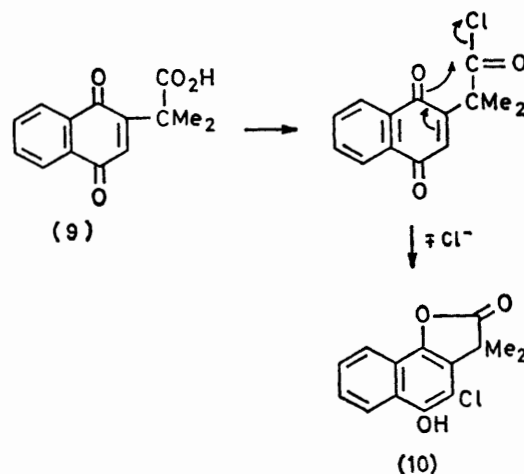
As expected, when the tribromoazo-acid (1;  $R^1 = R^2 = R^3 = Br$ ) reacted with thionyl chloride only the normal acid chloride was formed, and by subsequent reaction with methanol the methyl ester was obtained in 85% yield. However, when the 2,6-dimethylazo-acid (1;  $R^1 = R^2 = Me$ ,  $R^3 = H$ ) was allowed to react with thionyl chloride in the usual way it formed the *p*-chloroanilinobenzoxazinone (3;  $R^1 = R^2 = Me$ ,

$R^3 = Cl$ ) in 73% yield together with a small amount of the dichloro compound (5). This can be explained by *ipso*-chlorination, which is not unusual with aromatic methyl compounds<sup>6</sup> but would be sterically difficult in the tribromo case. Aromatisation of (6) would follow



SCHEME 3

with loss of Cl<sup>+</sup> (to form Cl<sub>2</sub> with Cl<sup>-</sup>) and intermolecular substitution by chlorine predominantly at C-4' and to a minor extent at C-7. The formation of some chlorine-free benzoxazinone (3;  $R^1 = R^2 = R^3 = H$ ) and its 7-monochloro derivative would also be expected; these



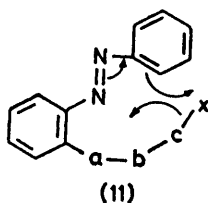
SCHEME 4

were not found but there was mass spectral evidence for the presence of the chlorine-free compound in the crude product. Further, when the reaction was carried out in carbon tetrachloride-anisole, *p*-chloroanisole was present in the product mixture.

The *ortho*-chlorination reaction (1)  $\rightarrow$  (3) is similar to the electrophilic *ortho*-chlorination of nitrones<sup>7</sup> by thionyl chloride (or phosgene) to give *o*-chloro-anil hydrochlorides (Scheme 3), and of *N*-arylhydroxamic acids (7) to form *o*-chloroarylamines (8), again with thionyl chloride<sup>8</sup> or phosgene. However, the chlorination which occurs<sup>9</sup> on reaction of the naphthoquinone-carboxylic acid (9) with thionyl chloride to give the lactone (10) is clearly intermolecular (Scheme 4).

In principle it should be possible to extend the *ortho*-chlorination (1)  $\rightarrow$  (3) to other *ortho*-substitution

reactions using other acid derivatives, and indeed other functional groups as expressed by (11).



#### EXPERIMENTAL

Spectra were measured for solutions in ethanol (u.v.) or  $\text{CDCl}_3$  (n.m.r.) and for Nujol mulls (i.r.). Petrol refers to light petroleum, b.p. 60–80 °C.

**2-(2-Arylazo-4-methylphenoxy)-2-methylpropanoic Acids (1).**—These were prepared from the appropriate azophenol (0.05 mol) (obtained by coupling *p*-cresol with a diazotised aniline) and chloretone (1,1,1-trichloro-2-methylpropan-2-ol) (0.1 mol equiv.) by the method of Corey *et al.*<sup>10</sup> They all showed  $\nu_{\text{max}}$  (CO) at 1720–1700 and HO at ca. 3300–2300  $\text{cm}^{-1}$ , and normal n.m.r. spectra [ $\delta(\text{CMe}_2)$  ca. 1.6]; phenylazo ( $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ), m.p. 80–81 °C (from petrol) (lit.,<sup>2</sup> 83–84 °C); 2-chlorophenylazo ( $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ), red needles, m.p. 116–117 °C (from petrol) (Found: C, 61.2; H, 5.3; Cl, 10.8; N, 8.6%;  $M^+$ , 332.0928.  $\text{C}_{17}\text{H}_{17}\text{ClN}_2\text{O}_3$  requires C, 61.4; H, 5.1; Cl, 10.7; N, 8.4%;  $M$ , 332.0927);  $\lambda_{\text{max}}$ , 235, 330, and 450sh nm (log  $\epsilon$  3.98, 4.10, and 2.87); 4-methylphenylazo ( $\text{R}^1 = \text{R}^2 = \text{H}$ ;  $\text{R}^3 = \text{Me}$ ), red needles, m.p. 93–95 °C (from petrol) (Found: C, 69.5; H, 6.7; N, 8.8%;  $M^+$ , 312.1470.  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3$  requires C, 69.2; H, 6.5; N, 9.0%;  $M$ , 312.1473);  $\lambda_{\text{max}}$ , 230sh, 330, and 440sh nm (log  $\epsilon$  3.05, 3.20, and 2.98); 4-methoxyphenylazo ( $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{OMe}$ ), red needles, m.p. 107–108 °C (from petrol) (Found: C, 65.6; H, 6.2; N, 8.4%;  $M^+$ , 328.1419.  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$  requires C, 65.8; H, 6.1; N, 8.5%;  $M$ , 328.1422);  $\lambda_{\text{max}}$ , 243, 357, and 444sh nm (log  $\epsilon$  3.93, 4.11, and 3.14); 4-nitrophenylazo ( $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{NO}_2$ ) red needles, m.p. 160–161 °C (from petrol) (Found: C, 59.3; H, 5.1; N, 12.3.  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_5$  requires C, 59.5; H, 5.0; N, 12.2%); 2,6-dimethylphenylazo ( $\text{R}^1 = \text{R}^2 = \text{Me}$ ,  $\text{R}^3 = \text{H}$ ), red needles, m.p. 109–111 °C (from petrol) (Found: C, 70.1; H, 7.1; N, 8.9%;  $M^+$ , 326.1630.  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3$  requires C, 69.9; H, 6.8; N, 8.6%;  $M$ , 326.1630);  $\lambda_{\text{max}}$ , 237sh, 320, and 460 nm (log  $\epsilon$  3.92, 3.99, and 2.78); 2,4,6-tribromophenylazo ( $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Br}$ ), red needles, m.p. 157–159 °C (from petrol) (Found: C, 38.0; H, 3.0; Br, 44.5; N, 5.3%;  $M^+$ , 531.8625.  $\text{C}_{17}\text{H}_{15}\text{Br}_3\text{N}_2\text{O}_3$  requires C, 38.2; H, 2.8; Br, 44.8; N, 5.2%;  $M$ , 531.8631);  $\lambda_{\text{max}}$ , 275sh, 303, 350sh, and 440sh nm (log  $\epsilon$  3.89, 3.97, 3.77, and 2.92).

When hydrogen chloride was passed through a solution of the phenylazo-acid (1;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ) (200 mg) in carbon tetrachloride (25 ml) for 2 h, and the mixture heated on a steam-bath under reflux for 1 h, and then evaporated, only unchanged acid was obtained.

**Reaction of the Azo-acids (1) with Thionyl Chloride.—General procedure.** The acid (1 mmol) and thionyl chloride (1 ml) were heating in refluxing carbon tetrachloride (20 ml) for 1 h, and the mixture was then evaporated. The residual oil was chromatographed on silica in chloroform to give the benzoxazinone (3). (In most of the benzoxazinone n.m.r. spectra the NH signal was not observed.)

The phenylazo-acid yielded 4-(2-chloroanilino)-2,2,6-

trimethyl-1,4-benzoxazin-3(2H)-one (3;  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ), needles, m.p. 184–185 °C (from benzene-petrol) (92%) (Found: C, 64.3; H, 5.2; Cl, 11.5; N, 9.0%;  $M^+$ , 316.0976.  $\text{C}_{17}\text{H}_{17}^{35}\text{ClN}_2\text{O}_2$  requires C, 64.5; H, 5.4; Cl, 11.2; N, 8.9%;  $M$ , 316.0978);  $\nu_{\text{max}}$ , 3310 and 1695  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ , 234sh and 290 nm (log  $\epsilon$  4.08 and 3.59);  $\delta$  7.45–6.52 (7 H, m, ArH), 2.27 (3 H, s, ArMe), and 1.54 (6 H, s,  $\text{CMe}_2$ ),  $\delta$  { $\text{CDCl}_3 + \text{Eu}([{}^2\text{H}_9]\text{fod})_3$ }; 9.95 (1 H, dd,  $J$  8 and 2 Hz, H-6' †), 9.17br (1 H, s, 5-H), 8.11 (1 H, d,  $J$  8 Hz, H-8), 7.65 (1 H, dd,  $J$  8 and 2 Hz, H-7), 7.33 (1 H, dd,  $J$  6 and 2 Hz, H-3' or -5'), 6.91 (1 H, dd,  $J$  8 and 2 Hz, H-5' or 3'), and 6.67 (1 H, t,  $J$  8 Hz, H-4'),  $m/e$  (%) 318(7), 316( $M^+$ , 22), 191(4), 190(9), 163(9), 162(79), 150(100), 148(21), 134(12), 127(13), 107(11), 99(13), 91(9), and 77(19); the *N*-acetyl derivative had m.p. 137–138 °C (from hexane) (Found: C, 63.8; H, 5.6; Cl, 9.8; N, 7.8%;  $M^+$ , 358.1083.  $\text{C}_{19}\text{H}_{19}^{35}\text{ClN}_2\text{O}_3$  requires C, 63.6; H, 5.3; Cl, 9.8; N, 7.8%;  $M$ , 358.1084);  $\nu_{\text{max}}$ , 1725 and 1695  $\text{cm}^{-1}$ ;  $\delta$  7.52–6.75 (7 H, m, ArH), 2.28 (3 H, s, ArMe), 2.15 (total 3 H, 2s,  $\text{CMe}_2$ ), 1.68 (3 H, s,  $\text{CMe}_2$ ), and 1.47 (total 3 H, 2s,  $\text{CMe}_2$ ) (2 conformers);  $\delta$  (PhCl; 30 °C) 2.14 (3 H, s), 2.01 (3 H, s), 1.64 (total 3 H, 2s), and 1.44 (total 3 H, 2s);  $\delta$  (PhCl, 80 °C), 2.14, 2.00, 1.61, and 1.47 (all 3 H, s). When this chlorination was repeated at room temperature for 30 min, followed by addition of boiling methanol (10 ml) and heating for 5 min, the products, isolated by chromatography on silica in petrol-chloroform (1 : 5), were the same benzoxazinone (39%) and the methyl ester of the starting acid identical (t.l.c., i.r.) with authentic material.

The 2-chlorophenylazo-acid afforded 4-(2,6-dichloroanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $\text{R}^1 = \text{R}^2 = \text{Cl}$ ,  $\text{R}^3 = \text{H}$ ), needles, m.p. 148–150 °C (from petrol) (92%) (Found: C, 58.1; H, 4.4; Cl, 20.6; N, 7.5%;  $M^+$ , 350.0590.  $\text{C}_{17}\text{H}_{16}^{35}\text{Cl}_2\text{N}_2\text{O}_2$  requires C, 58.1; H, 4.6; Cl, 20.5; N, 7.8%;  $M$ , 350.0588);  $\nu_{\text{max}}$ , 3293 and 1695  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ , 242sh and 293 nm (log  $\epsilon$  4.06 and 3.75);  $\delta$  7.40–6.77 (6 H, m, ArH), 2.33 (3 H, s, ArMe), and 1.49 (6 H, s,  $\text{CMe}_2$ );  $\delta$  { $\text{CDCl}_3 + \text{Eu}([{}^2\text{H}_9]\text{fod})_3$ }; 9.85br (1 H, s, H-5), 8.51 (1 H, d,  $J$  8 Hz, H-8), 7.91 (1 H, dd,  $J$  8 and 2 Hz, 7-H), 7.5 (2 H, d,  $J$  8 Hz, H-3' and -5'), and 6.91 (1 H, t,  $J$  8 Hz, 4'-H);  $m/e$  (%) 354(2), 352(14), 350( $M^+$ , 25), 191(16), 190(18), 165(45), 163(11), 162(35), 161(20), 150(100), and 148(26). Repeating this reaction using the acid (100 mg), thionyl chloride (0.2 ml), and anisole (500 mg) gave the same benzoxazinone (87%) and recovered anisole (89%); no anisole derivatives were detected (t.l.c.).

The 4-methylphenylazo-acid yielded 4-(2-chloro-4-methylanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ ), needles, m.p. 122–123 °C (from petrol) (98%) (Found: C, 65.2; H, 6.0; Cl, 10.9; N, 8.8%;  $M^+$ , 330.1134.  $\text{C}_{18}\text{H}_{19}^{35}\text{ClN}_2\text{O}_2$  requires C, 65.4; H, 5.8; Cl, 10.7; N, 8.5%;  $M$ , 330.1134);  $\nu_{\text{max}}$ , 3300 and 1695  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ , 232sh and 293 nm (log  $\epsilon$  4.31 and 3.75);  $\delta$  7.17–6.42 (6 H, m, ArH), 2.26 and 2.23 (each 3 H, s, ArMe), and 1.52 (6 H, s,  $\text{CMe}_2$ ),  $\delta$  { $\text{CDCl}_3 + \text{Eu}([{}^2\text{H}_9]\text{fod})_3$ }; 9.7 (1 H, d,  $J$  8 Hz, H-6'), 9.15br (1 H, s, H-5), 8.03 (1 H, d,  $J$  8 Hz, H-8), 7.53 (1 H, dd,  $J$  8 and 2.5 Hz, H-7), 6.95 (1 H, dd,  $J$  8 and 2.5 Hz, H-5), 6.82 (1 H, d,  $J$  2.5 Hz, H-3');  $m/e$  (%) 332(10), 330( $M^+$ , 32), 191(79), 176(14), 162(40), 150(100), 148(35), 142(18), 141(16), 140(71), 106(13), and 77(40); after reaction of this benzoxazin-3-one (165 mg) with thionyl chloride (0.5 ml) in boiling carbon tetrachloride (10 ml) for 1 h, the

\* fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato. † Primed numbers refer to the anilino-group throughout.

starting material was recovered and no dichloro-compound could be detected (t.l.c.).

The 4-methoxyphenylazo-acid after reaction with thionyl chloride at room temperature for 30 min gave 4-(2-chloro-4-methoxyanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{Cl}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OMe}$ ), needles, m.p. 153–154 °C (from petrol) (60%) (Found:  $M^+$ , 346.1083.  $\text{C}_{18}\text{H}_{19}^{35}\text{Cl-N}_2\text{O}_3$  requires  $M$ , 346.1086);  $\nu_{\text{max}}$ , 3 310 and 1 695  $\text{cm}^{-1}$ ;  $\delta$  7.4–6.4 (6 H, m, ArH), 3.72 (3 H, s, OMe), 2.28 (3 H, s, ArMe), and 1.52 (6 H, s,  $\text{CMe}_2$ );  $\delta$  { $\text{CDCl}_3 + \text{Eu}([\text{H}_9\text{fod}]_3)$ } 8.94 (1 H, d,  $J$  8 Hz, H-6'), 8.80br (1 H, s, H-5), 7.75 (1 H, d,  $J$  8 Hz, H-8), 7.43 (1 H, dd,  $J$  8 and 2.5 Hz, H-7), 6.64 (2 H, d,  $J$  2 Hz, H-3'), and 6.63 (1 H, dd,  $J$  10 and 2.5 Hz, H-5'),  $m/e$  (%) 346(6), 158(20), and 156(100).

The 2,6-dimethylphenylazo-acid yielded, after chromatography in petrol-chloroform (1 : 4), 4-(4-chloro-2,6-dimethylanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{R}^2 = \text{Me}$ ,  $R^3 = \text{Cl}$ ), needles, m.p. 169–170 °C (from petrol) (73%) (Found:  $C$ , 66.0; H, 5.8; Cl, 10.4; N, 8.3%;  $M^+$ , 344.1291.  $\text{C}_{19}\text{H}_{21}^{35}\text{ClN}_2\text{O}_2$  requires  $C$ , 66.2; H, 6.1; Cl, 10.3; N, 8.1%;  $M$ , 344.1290);  $\nu_{\text{max}}$ , 3 330 and 1 700  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ , 243 and 289 nm ( $\log \epsilon$  4.86 and 3.42),  $\delta$  7.38–6.85 (5 H, m, ArH), 6.10 (1 H, s, NH), 2.34 (3 H, s, ArMe), 2.22 (6 H, s, ArMe), and 1.46 (6 H, s,  $\text{CMe}_2$ );  $\delta$  { $\text{CDCl}_3 + \text{Eu}([\text{H}_9\text{fod}]_3)$ } 9.53br. (1 H, s, H-5), 8.11 (1 H, d,  $J$  8 Hz, H-8), 7.70 (1 H, dd,  $J$  8 and 2 Hz, H-7), and 7.04br (2 H, s, H-3' and -5');  $m/e$  (%) 346(3), 344( $M^+$ , 9), 191(60), 176(11), 156(28), 154(100), 150(21), 148(50), 91(45), and 77(32), and 7-chloro-4-(4-chloro-2,6-dimethylanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one, needles, m.p. 183–184 °C (from petrol) (3%) (Found:  $M^+$ , 378.0903.  $\text{C}_{19}\text{H}_{20}^{35}\text{Cl}_2\text{N}_2\text{O}_2$  requires  $M$ , 378.0901);  $\nu_{\text{max}}$ , 3 345 and 1 710  $\text{cm}^{-1}$ ;  $\delta$  7.6–6.0 (4 H, m, ArH), 2.35 (3 H, s, ArMe), 2.21 (6 H, s, ArMe), and 1.47 (6 H, s,  $\text{CMe}_2$ );  $\delta$  { $\text{CDCl}_3 + \text{Eu}([\text{H}_9\text{fod}]_3)$ } 8.91 (1 H, s, H-5), 7.91 (1 H, s, H-8), and 7.00br. (2 H, s, H-3' and -5');  $m/e$  (%) 378(3), 227(6), 225(25), 191(14), 184(10), 182(14), 156(24), 154(100), and 91(8). When a solution of this 2,6-dimethylphenylazo-acid (0.15 g) and thionyl chloride (0.5 g) in carbon tetrachloride (2 ml) and anisole (2 ml) was heated to 62 °C for 1 h *p*-chloroanisole was detected by g.l.c. among the products. When the experiment was repeated without the acid present *p*-chloroanisole was not detected.

The 2,4,6-tribromophenylazo-acid (267 mg) was heated with thionyl chloride (0.5 ml) in boiling carbon tetrachloride (10 ml) for 1 h. Evaporation left the crude acid chloride ( $\nu_{\text{CO}}$  1 790  $\text{cm}^{-1}$ ) to which methanol (10 ml) was added. Removal of solvent and distillation gave the methyl ester, b.p. 97–99 °C at 0.8 mmHg (85%) (Found:  $M^+$ , 545.8787.  $\text{C}_{18}\text{H}_{17}^{79}\text{Br}_3\text{N}_2\text{O}_3$  requires  $M$ , 545.8788);  $\nu_{\text{max}}$ , 1 740  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$ , 300 and 440sh nm ( $\log \epsilon$  3.71 and 3.01);  $\delta$  7.75–6.74 (5 H, m, ArH), 3.70 (3 H, s, OMe), 2.33 (3 H, s, ArMe), and 1.58 (6 H, s,  $\text{CMe}_2$ ).

4-(2-Chloroanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{Cl}$ ,  $R^2 = \text{R}^3 = \text{H}$ ).—To 2-methyl-2-(4-methyl-2-phenylazo)propanoic acid (333 mg) and 1M copper(II) sulphate (1 drop) in 95% hydrazine hydrate (2 ml) was added 30% hydrogen peroxide (1 ml), dropwise, at 0 °C. The solution was then poured into chloroform (50 ml), washed with 2M sodium hydroxide and water, dried ( $\text{MgSO}_4$ ), evaporated, and the residue chromatographed on silica in

chloroform to give 4-(2-chloroanilino)-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{Cl}$ ,  $R^2 = \text{R}^3 = \text{H}$ ), m.p. 185 °C (57%), identical with that described above.

This benzoxazinone (25 mg) in ethanol (20 ml) was hydrogenated over palladised charcoal at room temperature until uptake ceased. After removal of catalyst and solvent, the residue was chromatographed on silica in chloroform to give (a) starting material (a trace), (b) 4-anilino-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ), m.p. 134–135 °C (from petrol) (67%) (Found:  $C$ , 72.1; H, 6.3; N, 9.7%;  $M^+$ , 282.1369.  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4$  requires  $C$ , 72.3; H, 6.4; N, 9.8%;  $M$ , 282.1368);  $\nu_{\text{max}}$ , 3 303 and 1 690  $\text{cm}^{-1}$ ;  $\delta$  7.40–6.66 (8 H, m, ArH), 2.23 (3 H, s, ArMe), and 1.52 (6 H, s,  $\text{CMe}_2$ );  $m/e$  (%) 282( $M^+$ , 84), 191(17), 163(8), 162(940(1), 1500), 148(37), 134(14), 131(10), and 107(10), and 2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one, m.p. 169 °C (lit.<sup>2</sup> 153–154 °C) (from petrol) (25%) (Found:  $M^+$ , 191.0946. Calc. for  $\text{C}_{11}\text{H}_{13}\text{NO}_2$   $M$ , 191.0946);  $\nu_{\text{max}}$ , 3 200 and 1 680  $\text{cm}^{-1}$ ;  $\delta$  6.87–6.40 (3 H, m, ArH), 2.26 (3 H, s, ArMe), and 1.51 (6 H, s,  $\text{CMe}_2$ );  $m/e$  (%) 191( $M^+$ , 100), 176(25), 149(8), 148(79), 122(20), and 77(20). A similar hydrogenation of 2-methyl-2-(4-methyl-2-phenylazophenoxy)propanoic acid (500 mg) in ethanol (20 ml) over platinum oxide yielded (a) aniline (a trace) (t.l.c.), (b) 4-anilino-2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (3;  $R^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ) (10%), and (c) 2,2,6-trimethyl-1,4-benzoxazin-3(2H)-one (57%).

*Attempted Reactions with Azobenzene.*—(a) A mixture of 2-methyl-2-phenoxypropanoic acid (185 mg), azobenzene (182 mg), and thionyl chloride (0.5 ml) in carbon tetrachloride (15 ml) was heated under reflux for 3 h. There was no reaction (t.l.c.). (b) Under the same conditions no reaction with azobenzene was detected when it was heated with (i) benzoyl chloride, (ii) acetyl chloride, (iii) thionyl chloride, and (iv) benzoic acid and thionyl chloride.

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