2 : 3-*Dihydro*-3-*oxobenz*-1 : 4-*oxazines*.

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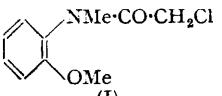
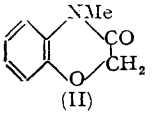
The action of aluminium chloride on α-chloroacyl-*o*-anisidides leads to 2 : 3-dihydro-3-oxobenz-1 : 4-oxazines and, in some cases, thence or directly to hydroxyoxindoles. Some reactions of the benzoxazines are described. The action of aluminium chloride on β-chloro-propion-*o*-anisidide and -*N*-methylpropion-*o*-anisidide, leading to 3 : 4-dihydrocarbostyrils, is examined. A satisfactory preparation of 2 : 4-dimethoxynitrobenzene is given.

It was shown by Cook, Loudon, and McCloskey (*J.*, 1952, 3904) that heating α-chloro-*N*-methylacet-*o*-anisidide (I) with aluminium chloride leads to the benzoxazine derivative (II) which at higher temperatures is rearranged to a mixture of 7- and 4-hydroxy-1-methyloxindole, (III) and (IV) respectively. The mixture was not separated into its components as such but, after methylation, the individual ethers were isolated and identified by independent syntheses. Almost at the same time Kretz, Muller, and Schlittler (*Helv. Chim. Acta*, 1952, 527) reported that the action of aluminium chloride on (I) gave much of (II) together with a hydroxy-1-methyloxindole which they regarded as (III). This conclusion, which overlooks the simultaneous formation of (III) and (IV), is obviously unsound and is, in fact, erroneous. The phenolic compounds (III) and (IV) are readily prepared by demethylation of their *O*-methyl ethers and we find that the properties of Kretz, Muller, and Schlittler's compound correspond with those of 4-hydroxy-1-methyloxindole (IV) and differ from those of (III).



(I)



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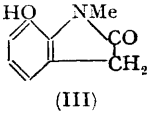

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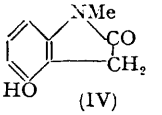

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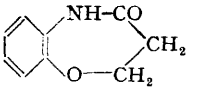

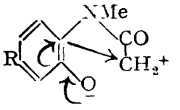

(VI)

The formation of benzoxazine derivatives from chloroacet-*o*-anisidides by reaction with aluminium chloride appears to be general. It proceeds through demethylation to *o*-chloroacetamidophenols which, in the absence of an *N*-alkyl substituent, are frequently isolatable and yield the benzoxazines by dissolution in aqueous alkali. A number of examples are described in the Experimental section. On the other hand, *o*-β-chloropropionamidophenol, obtained by demethylating β-chloropropion-*o*-anisidide, reacted with aqueous alkali to give a product which is regarded as *o*-acrylamidophenol rather than the isomeric 7-membered ring compound (V). This conclusion is based on the solubility of the product in alkali, on its ability to absorb 1 mol. of hydrogen and, more especially, on the similarity of the ultra-violet spectra obtained in presence and absence of alkali.

2 : 3-Dihydro-3-oxobenz-1 : 4-oxazine (II; H for Me) is readily *N*-methylated by methyl sulphate and alkali but, in general, methylation is best achieved by using methyl iodide and powdered potassium hydroxide in acetone (cf. Pachter and Kloetzal, *J. Amer. Chem. Soc.*, 1952, **74**, 1321). Both the parent compound and its *N*-methyl derivative (II) contain reactive—albeit feebly reactive—methylene groups as is shown by the formation of benzylidene derivatives. As a cyclic amide, (II) is readily reduced by lithium aluminium hydride, forming 2 : 3-dihydro-4-methylbenz-1 : 4-oxazine. The convertibility of 2 : 3-dihydro-3-oxobenzoxazines into hydroxyoxindoles is restricted in practice by the high temperature (200—220°) required for the reaction and also by the need for a 4(*N*)-substituent. Thus we have confirmed (cf. Cook *et al.*, *loc. cit.*) that neither 2 : 3-dihydro-3-oxobenz-1 : 4-oxazine nor its 2-methyl derivative yields oxindoles in appreciable amount, whereas (II) yields (III) and (IV), and 2 : 3-dihydro-2 : 4-dimethyl-3-oxobenz-1 : 4-oxazine

affords 7-hydroxy-1 : 3-dimethyloxindole. In this last reaction no isomeric product, corresponding to the transformation of (II) into (IV), was detected and the structure of the isolated product was established by its conversion into 7-methoxy-1 : 3-dimethylindole which was independently synthesised. If the change from (II) to (IV) involves the mechanism briefly indicated by (VI), it should be promoted where the substituent R is an electron-donor. However, 2 : 3-dihydro-7-hydroxy-4-methyl-3-oxobenz-1 : 4-oxazine, which was synthesised to test this view, proved to be too unstable under the conditions for isomerisation. Thereby, like its 6-hydroxy-isomer and also like 2 : 3-dihydro-4-methyl-3-oxonaphth(2′ : 1′-2 : 3)-1 : 4-oxazine (cf. Lees and Shedden, *J.*, 1903, **83**, 758), it was converted into an intractable, highly coloured, and amorphous powder.

Under favourable conditions the hydroxyoxindoles (III) and (IV) are directly produced by the action of aluminium chloride on (I) without isolation, and possibly without intermediate formation, of the benzoxazine (II). The reaction is thus a particular case of Stollé's oxindole synthesis (*J. pr. Chem.*, 1930, **128**, 1; cf. Abramovitch and Hey, *J.*, 1954, 1697) which is known to give optimum results when the α-chloroacylaniline used carries an *N*-alkyl substituent (see Julian in Elderfield's "Heterocyclic Compounds," Wiley, New York, 1952, Vol. III, p. 144). On the other hand, 3 : 4-dihydrocarbostyrils are readily prepared by the action of aluminium chloride at relatively low temperatures on β-chloropropionanilides whether *N*-alkylated or not (Mayer, Zütphen, and Philipps, *Ber.*, 1927, **60**, 858). The latter reaction was therefore examined with the β-chloropropionyl derivatives of *o*-anisidine and *N*-methyl-*o*-anisidine. In each case a single product was obtained and was identified as 3 : 4-dihydro-8-hydroxycarbostyril and its *N*-methyl derivative respectively. For identification, the products, after *O*-methylation and reduction, were converted into suitable derivatives of 1 : 2 : 3 : 4-tetrahydro-8-methoxyquinoline.

2 : 4-Dimethoxynitrobenzene, hitherto surprisingly inaccessible, was prepared from resorcinol dimethyl ether either by successive sulphonation and nitration or, better, by direct nitration using copper nitrate in acetic anhydride.

Experimental

General Procedures.—*N*-Acylation of amines was effected by adding the acid chloride (0·1 mole) slowly to a cooled, stirred solution of the amine (0·1 mole) and pyridine (0·1 mole) in benzene (500 c.c.), and after 24 hr. at room temperature the amide was recovered from the acid-washed, dried, benzene solution. For *N*-methylation of amides, both cyclic and acyclic, methyl iodide (0·15 mole) was added in two portions (10-min. interval) to a gently boiling suspension of powdered potassium hydroxide (0·25 mole) in acetone (350 c.c.; "AnalaR") containing the amide (0·1 mole); heating was continued for 20 min. and the product was recovered by concentrating the solution and adding water (cf. Pachter and Kloetzal, *loc. cit.*). Preferential *O*-methylation of phenolic amides was similarly effected by using potassium carbonate (0·25 mole) in place of the hydroxide and heating under reflux for 6 hr. Fusion with aluminium chloride was carried out by heating the mixed, powdered reagents with stirring at the temperature and for the time stated, followed by decomposition of the cooled, powdered product with iced hydrochloric acid and subsequent treatment as described.

2 : 3-Dihydro-3-oxobenz-1 : 4-oxazine, m. p. 171—172° (from water), was prepared (*a*) by hydrogenating *o*-nitrophenoxyacetic acid (Minton and Stephen, *J.*, 1922, **121**, 1591) in acetic acid with palladium as catalyst, being obtained almost quantitatively from the filtered and concentrated solution; (*b*) by fusing chloroacet-*o*-anisidide with aluminium chloride at 180° for 1 hr. (cf. Cook, Loudon, and McCloskey, *loc. cit.*). By the latter procedure at a lower temperature (80—100°; 30 min.) the main product was *o*-chloroacetamidophenol, m. p. 135·5—136·5° (from benzene) (Found: C, 51·4; H, 4·3; N, 7·7. Calc. for $C_8H_8O_2NCl$: C, 51·8; H, 4·3; N, 7·55%) (Aschan, *Ber.*, 1887, **20**, 1524, gives m. p. 136° for the compound as prepared from *o*-aminophenol), and this by dissolution in alkali was converted into the oxazine. Moreover, when the pre-formed oxazine was fused with aluminium chloride at 220° for 20 min. it afforded a solid, m. p. 114—115° (from water) (Found: C, 57·3; H, 5·0%), which appears to be a mixture of *o*-chloroacetamidophenol and unchanged oxazine since it (i) had mixed m. p. 125—128° with the former compound and (ii) gave the oxazine, m. p. 167—171°, when recovered by evaporation from 2N-hydrochloric acid. Auwers and Fries (*Ber.*, 1926, **59**, 539) obtained a similar product, m. p. 114—115°, which they regarded as an allotropic modification of *o*-chloro-

acetamidophenol, by the action of chloroacetyl chloride on *o*-aminophenol in weakly alkaline solution (wherein some formation of the oxazine is to be expected).

2 : 3-Dihydro-3-oxobenz-1 : 4-oxazine had light absorption (in EtOH) : $\lambda_{max.}$ 2550, 2860 Å (log ε, 3·73, 3·59). It is slightly soluble in aqueous alkali and yields the 4-methyl derivative (see below) by treatment with methyl sulphate in sodium hydroxide. When it (1·5 g.) was heated (8 hr.) with benzaldehyde (1·1 g.) and acetic anhydride (3·1 g.) in presence of fused sodium acetate, and the whole was then added to water, the recovered oil afforded as neutral fraction *2-benzylidene-2 : 3-dihydro-3-oxobenz-1 : 4-oxazine* which formed pale yellow needles, m. p. 260—261° (from ethanol) (Found : C, 75·9; H, 5·0; N, 6·2. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·7; N, 5·9%) : light absorption (in EtOH), $\lambda_{max.}$ 2570, 3350 Å (log ε 4·19, 4·29). Catalytic hydrogenation of this compound in acetic acid with palladium as catalyst afforded *2-benzyl-2 : 3-dihydro-3-oxobenz-1 : 4-oxazine*, m. p. 159° (from light petroleum, b. p. 60—80°) (Found : C, 74·8; H, 4·9; N, 6·1. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·85%) : light absorption (in EtOH) : $\lambda_{max.}$ 2520, 2810 Å (log ε 3·83, 3·66).

2 : 3-Dihydro-4-methyl-3-oxobenz-1 : 4-oxazine, m. p. 58° (from light petroleum, b. p. 60—80°), was prepared (*a*) in 90% yield by *N*-methylation of the foregoing oxazine; (*b*) as described by Cook, Loudon, and McCloskey (*loc. cit.*) from anisidine—but by the general procedures given here—*via α-chloro-N-methylacet-o-anisidide* which was now obtained as rods, m. p. 49—50° (from light petroleum, b. p. 40—60°) (Found : C, 56·35; H, 5·5. $C_{10}H_{12}O_2NCl$ requires C, 56·2; H, 5·7%), and afforded the oxazine, m. p. 57—58°, when fused with aluminium chloride at 180° for 1 hr. The oxazine had light absorption (in EtOH) : $\lambda_{max.}$ 2540, 2850 Å (log ε 3·78, 3·64). It (0·8 g.) condensed with benzaldehyde (0·53 g.) when they were heated (12 hr.) together in benzene (25 c.c. in presence of powdered sodamide (0·3 g.) affording *2-benzylidene-2 : 3-dihydro-4-methyl-3-oxobenz-1 : 4-oxazine* as yellow needles, m. p. 155—156° (from ethanol) (Found : C, 76·2; H, 5·35; N, 5·8. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2; N, 5·6%) : light absorption (in EtOH) : $\lambda_{max.}$ 2700, 3370 Å (log ε 4·15, 4·28). The corresponding benzyl compound, as prepared by catalytic hydrogenation, did not solidify.

2 : 3-Dihydro-4-methylbenz-1 : 4-oxazine, b. p. 61°/5 × 10^{-5} mm. (Knorr, *Ber.*, 1889, **22**, 2081, gives b. p. 261°/760 mm.), was obtained when the foregoing 3-oxo-derivative (5 g.) and lithium aluminium hydride (2 g.) were allowed to react in anhydrous ether (200 c.c.) during 3 days and the washed and dried ether solution was evaporated. It formed a *picrate*, m. p. 149—150° (from ethanol) (Found : C, 47·7; H, 4·0; N, 14·95. $C_9H_{11}ON,C_6H_3O_7N_3$ requires C, 47·6; H, 3·7; N, 14·8%), a hydrochloride, m. p. 168—169° (from ethanol) (Found : C, 58·3; H, 6·25; N, 7·6. Calc. for $C_9H_{11}ON,HCl$: C, 58·2; H, 6·5; N, 7·55%), and a methiodide, m. p. 198—200° (decomp.) (from methanol). For the last two derivatives Lees and Shedden (*loc. cit.*) give m. p.s 167—167° and 195—200°, respectively. Light absorption of the hydrochloride (in EtOH) : $\lambda_{max.}$ 2580, 2980 Å (log ε 3·82, 3·56).

4- and 7-Hydroxy-1-methyloxindole.—α-Chloro-*N*-methylacet-*o*-anisidide (3 g.) was fused with anhydrous aluminium chloride (4 g.) at 220° for 1 hr. and the phenolic products (2·1 g.) were *O*-methylated in acetone, affording a mixture of 4- and 7-methoxy-1-methyloxindole, which was purified by distillation and separated by preferential extraction of the latter isomer in ether (cf. Cook *et al.*, *loc. cit.*). Light absortion (in EtOH) of 4-methoxy-1-methyloxindole (m. p. 137°), $\lambda_{max.}$ 2510, 2810 Å (log ε 3·67, 3·32); of 7-methoxy-1-methyloxindole (m. p. 102°), $\lambda_{max.}$ 2530, 2950 Å (log ε, 3·95, 3·50). When fused with aluminium chloride (0·4 g.) at 120° for 30 min. the 4-methoxy-isomer (0·2 g.) afforded *4-hydroxy-1-methyloxindole*, m. p. 230—232° (from water) : light absorption (in EtOH) : $\lambda_{max.}$ 2520, 2800 Å (log ε 3·83, 3·37) (Found : C, 66·1; H, 5·5. $C_9H_9O_2N$ requires C, 66·2; H, 5·6%). Similarly the 7-methoxy-isomer gave *7-hydroxy-1-methyloxindole*, m. p. 275—277°; light absorption (in EtOH) : $\lambda_{max.}$ 2450, 2860 Å (log ε 3·82, 3·52) (Found : C, 66·0; H, 5·6%). The former hydroxy-isomer corresponds in m. p. with that (m. p. 227—228°) recorded by Kretz, Muller, and Schlittler (*loc. cit.*), and of the two isomers it alone gave a dye of the rhodamine type when fused with phthalic anhydride and zinc chloride.

2 : 3-Dihydro-2 : 4-dimethyl-3-oxobenz-1 : 4-oxazine.—α-Chloropropion-*o*-anisidide (34 g.), obtained as a light yellow oil from *o*-anisidine and α-chloropropionyl chloride, was fused with aluminium chloride (30 g.) at 120° (30 min.). The phenolic product was dissolved in dilute aqueous sodium hydroxide (250 c.c.) from which 2 : 3-dihydro-2-methyl-3-oxobenz-1 : 4-oxazine crystallised as needles, m. p. and mixed m. p. 143—144° (from benzene) (cf. Cook *et al.*, *loc. cit.*). *N*-Methylation of this oxazine afforded *2 : 3-dihydro-2 : 4-dimethyl-3-oxobenz-1 : 4-oxazine* also as needles, m. p. 49·5—50° (from light petroleum, b. p. 40—60°) (Found : C, 67·5; H, 6·0. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·3%). Light absorption (in EtOH) : $\lambda_{max.}$ 2550, 2860 Å (log ε 4·01, 3·9).

7-*Hydroxy*-1 : 3-*dimethyloxindole*.—2 : 3-Dihydro-2 : 4-dimethyl-3-oxobenz-1 : 4-oxazine (5 g.) was fused with aluminium chloride (10 g.) at 220° (1 hr.) and the phenolic product (4·5 g.), after purification in methanol on a charcoal column, gave 7-*hydroxy*-1 : 3-*dimethyloxindole* as prisms, m. p. 224—226° (from methanol) (Found : C, 67·6; H, 6·6; N, 7·55. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·3; N, 7·9%). Light absorption (in EtOH) : $\lambda_{max.}$ 2490, 2970 Å (log ε 3·87, 3·57). The oil obtained by *O*-methylation of this compound in acetone was distilled at 146—148°/9·8 × 10^{-2} mm., affording a solid distillate of 7-*methoxy*-1 : 3-*dimethyloxindole*, needles, m. p. 65—66° (from light petroleum, b. p. 40—60°) (Found : C, 68·9; H, 6·55; N, 7·5. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%). Light absorption (in EtOH) : $\lambda_{max.}$ 2520, 2930 Å (log ε, 3·92, 3·5).

7-*Methoxy*-1 : 3-*dimethylindole*.—(*a*) The foregoing oxindole (0·5 g.) was reduced (5 hr. at room temperature) with lithium aluminium hydride (0·2 g.) in dry ether (25 c.c.). The solid obtained, after being washed first with water, then with dilute hydrochloric acid and recovered by evaporation of the dried ethereal layer, afforded 7-*methoxy*-1 : 3-*dimethylindole* as rhombs, m. p. 68—69° (from light petroleum, b. p. 40—60°) (Found : C, 75·5; H, 7·1; N, 8·65. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5; N, 8·0%). Light absorption (in EtOH) : $\lambda_{max.}$ 2260, 2730, 2880, 3000 Å (log ε 4·69, 3·74, 3·78, 3·78). The compound, which gave a positive Ehrlich reaction, formed a *picrate* as chocolate-brown needles, m. p. 163—164° (from ethanol) Found : C, 50·3; H, 3·8; N, 14·1. $C_{11}H_{13}ON,C_6H_3O_7N_3$ requires C, 50·5; H, 4·0; N, 13·9%). The acid washings of the foregoing ethereal extract, after basification, recovery in ether, and addition of an ethereal solution of picric acid, afforded 7-*methoxy*-1 : 3-*dimethylindoline picrate* as yellow plates, m. p. 135—136° (from ethanol) (Found : C, 50·6; H, 4·8; N, 13·95. $C_{11}H_{15}ON,C_6H_3O_7N_3$ requires C, 50·25; H, 4·5; N, 13·8%).

(*b*) A solution of 7-methoxy-3-methylindole (1·2 g.) (Cook *et al.*, *loc. cit.*) in ether (10 c.c.) was slowly added with stirring at −40° to a solution of potassium (0·29 g.) in liquid ammonia (*ca.* 25 c.c.) containing a crystal of ferric nitrate. Then methyl iodide (1·1 g.) in ether (10 c.c.) was added and, after 45 min. at −40°, the solvent was allowed to evaporate, and the residue in light petroleum (b. p. 40—60°) was passed through a column of alumina; the early eluate afforded 7-methoxy-1 : 3-dimethylindole, m. p. and mixed m. p. with the previous sample 69—70° (picrate, m. p. and mixed m. p. 162—163°).

2 : 4-*Dimethoxynitrobenzene*.—(*a*) Concentrated sulphuric acid (20 c.c.) was slowly added to a solution of resorcinol dimethyl ether (20 g.) in acetic acid (100 c.c.), and the whole was then warmed to 70° to complete the reaction. The cooled solution was diluted with water (20 c.c.), treated with concentrated nitric acid (20 c.c.; *d*, 1·42), and left overnight at room temperature. Water (750 c.c.) was added and the whole was extracted with benzene, the extract being washed with dilute sodium hydroxide solution, dried, and passed through a column of alumina, from which the product was readily eluted. 2 : 4-Dimethoxynitrobenzene was recovered from the eluate as colourless plates, m. p. 74° (30% yield).

(*b*) Resorcinol dimethyl ether (10 g.) was slowly stirred into a mixture of copper nitrate (10 g.) and acetic anhydride (30 g.) kept below 25°. After 4 hr. the whole was added to water (300 c.c.) and the resultant solid was collected and purified as in (*a*) (70% yield).

2 : 3-*Dihydro*-7-*hydroxy*-3-*oxobenz*-1 : 4-*oxazine*.—2 : 4-Dimethoxyaniline was obtained as a colourless oil, b. p. 75—80°/6 × 10^{-3} mm., by hydrogenating 2 : 4-dimethoxynitrobenzene in acetic acid with palladium as catalyst. The derived α-chloro-2 : 4-dimethoxyacetanilide (2 g.), m. p. 90° (Heidelberger and Jacobs, *J. Amer. Chem. Soc.*, 1919, **41**, 1469, give m. p. 90°), when fused with aluminium chloride (10 g.) and sodium chloride (4 g.) at 140° (15 min.), afforded α-*chloro*-2 : 4-*dihydroxyacetanilide*, m. p. 179—180° (from water) (Found : C, 47·9; H, 4·3; N, 7·3. $C_8H_8O_3NCl$ requires C, 47·7; H, 4·0; N, 7·0%). This compound was dissolved in dilute sodium hydroxide solution and after 1 hr. the solution was acidified, saturated with ammonium sulphate, and extracted with ether, from which 2 : 3-*dihydro*-7-*hydroxy*-3-*oxobenz*-1 : 4-*oxazine* was recovered and formed colourless needles, m. p. 208—209° (from water) (Found : C, 58·2; H, 4·5; N, 8·6. $C_8H_7O_3N$ requires C, 58·2; H, 4·3; N, 8·5%). Light absorption (in EtOH) : $\lambda_{max.}$ 2680 Å; log ε, 3·91; inflexion, 2840—2920 Å (log ε 3·77—3·72). In ice-cold dilute sodium hydroxide it reacted with acetic anhydride, forming the 7-*acetoxy*-derivative, m. p. 216—217° (from water) (Found : C, 58·0; H, 4·2; N, 6·8. $C_{10}H_9O_4N$ requires C, 58·0; H, 4·4; N, 6·8%).

2 : 3-*Dihydro*-7-*hydroxy*-4-*methyl*-3-*oxobenz*-1 : 4-*oxazine*.—2 : 4-Dimethoxy-*N*-methylacetanilide, obtained as an oil by *N*-methylation of 2 : 4-dimethoxyacetanilide (the latter had m. p. 116°; Vermeulen, *Rec. Trav. chim.*, 1919, **38**, 109, gives m. p. 117°), was hydrolysed by hot 30% sulphuric acid, affording 2 : 4-dimethoxy-*N*-methylaniline, b. p. 66—68°/3 × 10^{-4} mm., and this was characterised as the *benzoyl* derivative, m. p. 173—174° (from ethanol) (Found :

C, 70·6; H, 6·0; N, 5·3. $C_{16}H_{17}O_3N$ requires C, 70·8; H, 6·3; N, 5·2%). The corresponding chloroacetyl derivative was solid at 0° but without purification it (2 g.) was fused with aluminium chloride (10 g.) and sodium chloride (4 g.) at 140° (½ hr.) affording, after recovery, 2 : 3-*dihydro*-7-*hydroxy*-4-*methyl*-3-*oxobenz*-1 : 4-*oxazine* as needles, m. p. 180—182° (from water : charcoal) (Found : C, 60·6; H, 5·3; N, 8·1. $C_9H_9O_3N$ requires C, 60·3; H, 5·1; N, 7·8%). Light absorption (in EtOH) : $\lambda_{max.}$ 2640, 2890 Å (log ε 3·90, 3·78).

2 : 3-*Dihydro*-6-*hydroxy*-3-*oxobenz*-1 : 4-*oxazine*.—α-*Chloro*-2 : 5-*dimethoxyacetanilide*, m. p. 76—77° (from light petroleum, b. p. 60—80°), was prepared from 2 : 5-dimethoxyaniline and chloroacetyl chloride (Found : C, 53·1; H, 5·0; N, 6·4. $C_{10}H_{12}O_3NCl$ requires C, 52·4; H, 5·3; N, 6·1%). It was also regenerated, by the action of ethereal diazomethane, from α-*chloro*-2 : 5-*dihydroxyacetanilide*, m. p. 196—197° (from water) (Found : C, 47·8; H, 3·9; N, 6·9. $C_8H_8O_3NCl$ requires C, 47·7; H, 4·0; N, 6·95%), to which it gave rise when heated with aluminium chloride and sodium chloride at 140° (10 min.). When the dihydroxy-compound was just brought into solution in dilute aqueous sodium hydroxide a transient green colour appeared and changed to brown while a brown solid was deposited. This solid was collected and combined with material recovered in ether from the acidified solution, affording 2 : 3-*dihydro*-6-*hydroxy*-3-*oxobenz*-1 : 4-*oxazine* as colourless needles, m. p. 249—250° (from water : charcoal) (Found : C, 58·3; H, 4·4; N, 8·2. $C_8H_7O_3N$ requires C, 58·2; H, 4·3; N, 8·5%). Light absorption (in EtOH) : $\lambda_{max.}$ 3020 Å (log ε 3·69); inflexion, 2500—2600 Å (log ε 3·54—3·48). It afforded the 6-*acetoxy*-derivative, m. p. 162° (from water) (Found : C, 58·6; H, 4·7; N, 6·9. $C_{10}H_9O_4N$ requires C, 58·0; H, 4·4; N, 6·8%), but attempted *O*-methylation gave the *ON*-dimethyl derivative, m. p. and mixed m. p. 76—77° (see below).

2 : 3-*Dihydro*-6-*hydroxy*-4-*methyl*-3-*oxobenz*-1 : 4-*oxazine*.—2 : 5-Dimethoxy-*N*-methylaniline, b. p. 70°/1·8 × 10^{-4} mm., obtained from 2 : 5-dimethoxyacetanilide by *N*-methylation and subsequent hydrolysis, reacted with chloroacetyl chloride forming α-*chloro*-2 : 5-*dimethoxy*-N-*methylacetanilide*, m. p. 67—68° (from light petroleum, b. p. 40—60°) (Found : C, 54·5; H, 5·4; N, 6·2. $C_{11}H_{14}O_3NCl$ requires C, 54·3; H, 5·75; N, 5·8%). This compound (1 g.) was fused with aluminium chloride (5 g.) and sodium chloride (2 g.) at 140° (15 min.), affording 2 : 3-*dihydro*-6-*hydroxy*-4-*methyl*-3-*oxobenz*-1 : 4-*oxazine* as colourless needles, m. p. 209° (from water) (Found : C, 60·4; H, 4·9; N, 8·0. $C_9H_9O_3N$ requires C, 60·3; H, 5·1; N, 7·8%). Light absorption (in EtOH) : $\lambda_{max.}$ 3030 Å (log ε 3·72), inflexion, 2500—2600 Å (log ε 3·58—3·46). On acetylation it formed the 6-*acetoxy*-derivative, m. p. 93—94° (from water) (Found : C, 59·6; H, 4·7; N, 6·6. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0; N, 6·3%), and on methylation gave the 6-*methoxy*-derivative, m. p. 77—78° (from light petroleum, b. p. 60—80°) (Found : C, 62·5; H, 5·7; N, 7·5. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·25%). Light absorption for the 6-methoxy-compound (in EtOH) : $\lambda_{max.}$ 3000 Å (log ε, 3·73); inflexion, 2440—2580 Å (log ε 3·60—3·50).

2 : 3-*Dihydro*-5-*methyl*-3-*oxobenz*-1 : 4-*oxazine*.—Chloroacetic acid (14·6 g.) was added to a boiling solution of 2-nitro-*m*-cresol (21·5 g.) and sodium hydroxide (12·4 g.) in water (200 c.c.) and, after 3 hr. at 100°, unchanged nitrocresol was removed in steam. Acidification of the residual solution afforded 3-*methyl*-2-*nitrophenoxyacetic acid*, m. p. 194—196° (from water) (Found : C, 51·45; H, 4·3. $C_9H_9O_5N$ requires C, 51·2; H, 4·3%). This was hydrogenated over palladium in acetic acid, yielding 2 : 3-*dihydro*-5-*methyl*-3-*oxobenz*-1 : 4-*oxazine* as needles, m. p. 188—190° (from water) (Found : C, 66·5; H, 5·7. $C_9H_9O_2N$ requires C, 66·25; H, 5·6%). *N*-Methylation of this oxazine gave 2 : 3-*dihydro*-4 : 5-*dimethyl*-3-*oxobenz*-1 : 4-*oxazine* as plates, m. p. 86—87° (from light petroleum, b. p. 60—80°) (Found : C, 67·7; H, 6·1. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·3%).

β-*Chloropropion*-o-*anisidide*, m. p. 68° (from light petroleum, b. p. 40—60°), was prepared from *o*-anisidine and β-chloropropionyl chloride (Found : C, 56·3; H, 5·6; N, 6·4. $C_{10}H_{12}O_2NCl$ requires C, 56·2; H, 5·7; N, 6·6%). When fused with aluminium chloride at 130° (10 min.) it afforded *o*-β-chloropropionamidophenol, m. p. 122—123° from benzene (charcoal) (Found : C, 54·1; H, 5·2; N, 7·2. Calc. for $C_9H_{10}O_2NCl$: C, 54·1; H, 5·05; N, 7·0%); Mayer *et al.* (*loc. cit.*) give m. p. 125°. A solution of this phenol in dilute aqueous sodium hydroxide was left for 2 hr. at room temperature, then acidified and extracted with ether. The recovered oil solidified when rubbed with benzene, affording *o*-*acrylamidophenol* as leaflets, m. p. 122—123° (from benzene) (Found : C, 66·5; H, 5·85; N, 8·8; F, 1·04, by micro-hydrogenation in acetic acid over palladium. $C_9H_9O_2N$ requires C, 66·25; H, 5·7; N, 8·6%). Light absorption (in EtOH) $\lambda_{max.}$ 3000 Å (log ε, 3·9); (in NaOH) 2330, 3280 Å (log ε 4·6, 3·78); (in EtOH–NaOEt) 2400, 3000 Å (log ε 3·89, 3·82).

3 : 4-Dihydro-8-hydroxycarbostyril, m. p. 194° (Mayer *et al.*, *loc. cit.*, give m. p. 195°), was obtained by fusing β-chloropropion-*o*-anisidide (5 g.) with aluminium chloride (10 g.) at 220°

(1 hr.) (Found: C, 66·4; H, 5·7; N, 8·4. Calc. for $C_9H_9O_2N$: C, 66·2; H, 5·7; N, 8·6%). On methylation it afforded 3 : 4-*dihydro*-8-*methoxycarbostyril* as irregular prisms, m. p. 97—98° (from light petroleum, b. p. 60—80°) (Found: C, 68·0; H, 6·4; N, 8·1. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·3; N, 7·9%): light absorption (in EtOH): $\lambda_{max.}$ 2500, 2840 Å (log ε 4·00, 3·58). Reduction of this compound (0·6 g.) with lithium aluminium hydride (0·3 g.) in ether (50 c.c.) yielded, after 2 hr., 1 : 2 : 3 : 4-tetrahydro-8-methoxyquinoline which was identified as the benzoyl derivative, m. p. 132° undepressed by admixture with a specimen prepared by reduction of 8-methoxyquinoline (Tröger and Krückeberg, *J. pr. Chem.*, 1926, **114**, 249, give m. p. 136°).

3 : 4-*Dihydro*-8-*hydroxy*-1-*methylcarbostyril*.—To the oily β-chloro-*N*-methyl-*o*-propionanisidide (2 g.), prepared from *N*-methyl-*o*-anisidine and β-chloropropionyl chloride, anhydrous aluminium chloride (4 g.) was added, and the mixture heated at 110° for 1 hr. After recovery, 3 : 4-*dihydro*-8-*hydroxy*-1-*methylcarbostyril* was obtained as needles, m. p. 195—196° (from benzene) (Found: C, 68·0; H, 6·55; N, 7·8. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·3; N, 7·9%). Light absorption (in EtOH): $\lambda_{max.}$ 2490, 2890 Å (log ε 3·96, 3·67). On methylation the compound formed 3 : 4-*dihydro*-8-*methoxy*-1-*methylcarbostyril*, m. p. 86° (from light petroleum, b. p. 40—60°) (Found: C, 69·15; H, 6·8; N, 7·4. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%): light absorption (in EtOH): $\lambda_{max.}$ 2510, 2900 Å (log ε 4·07, 3·73). Reduction of this compound (0·5 g.) with lithium aluminium hydride (0·3 g.) in ether (75 c.c.) yielded, after 5 hr., 1 : 2 : 3 : 4-tetrahydro-8-methoxy-1-methylquinoline, identified as its chloroplatinate, m. p. 198° (decomp.) from water [Fischer and Köhn, *Ber.*, 1886, **19**, 1040, give m. p. 199° (decomp.)].

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