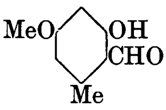
CCCXXXIII.—*Derivatives of Orcinol. Part I.*

By EDMUND LANGLEY HIRST.

IT has become apparent, during investigations which are now in progress into the structure of certain members of the group of lichen acids, that special importance must be attached to the isomeric orcylaldehyde monomethyl ethers as intermediate substances in synthetic work. It was therefore deemed advisable as a preliminary step to obtain further and more definite chemical evidence concerning the orientation of these two isomerides. This stituted derivatives of acetophenone. Under the appropriate conditions, orcylaldehyde 5-methyl ether (I) would be expected to yield pyrylium salts directly, in the same manner as does resorcylaldehyde (compare Perkin and Robinson, P., 1907, **19**, 149; Decker and von Fellenberg, *Ber.*, 1907, **40**, 3815), whereas the isomeric 3-methyl ether (II) could not do so. When the experiment was made, the orcylaldehyde monomethyl ether (m. p. 188°) described by Gattermann (*Annalen*, 1907, **357**, 346) failed to yield a pyrylium salt either with acetophenone or with acetylanisole, whilst with the latter reagent in the presence of alkali it gave the unsaturated *ketone* (III), which did not give a pyrylium salt until demethylation had been effected by means of hydriodic acid.

The orientation of the original substance as orcylaldehyde 3-methyl ether (4-hydroxy-2-methoxy-6-methylbenzaldehyde), which was previously proposed by Gattermann, is thus confirmed. On the other hand, the isomeric orcylaldehyde monomethyl ether (everninaldehyde; Hoesch, *Ber.*, 1913, **46**, 886) readily formed pyrylium salts when condensed with acetophenone in an acid medium and it must accordingly be orcylaldehyde 5-methyl ether (I).

(I.)



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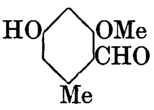

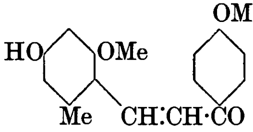

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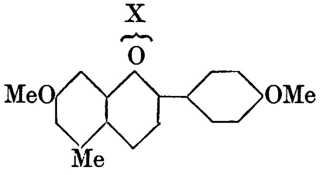

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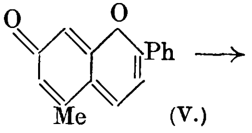

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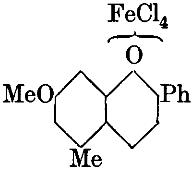
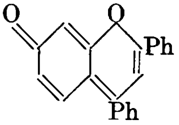




(VII.)

Amongst the compounds investigated, the 4′ : 7-dimethoxy-2-phenyl-5-methylbenzopyrylium salts (IV) obtained from everninaldehyde and acetylanisole were remarkable for their exceedingly intense powers of fluorescence; qualitative comparisons of pyrylium salts from the two orcylaldehyde monomethyl ethers and from orcylaldehyde indicated that the greatly enhanced fluorescent activity of the 4′ : 7-dimethoxy-compounds is connected with the simultaneous presence of the two methoxy-groups in the molecule, The properties and behaviour of all the compounds examined were strictly normal and comparable with those of pyrylium salts prepared from resorcylaldehyde or similar substances. Details will be found in the experimental section.

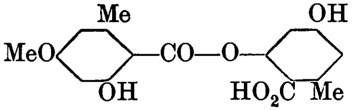
Attempts to prepare the bases corresponding to these pyrylium salts led in each case to the isolation of the anhydro-base. Very few of these compounds have hitherto been examined in detail on account of the difficulty experienced in obtaining them in a crystalline condition, and in the present work only one anhydro-base has been made to crystallise : 7-*hydroxy*-2-*phenyl*-5-*methylbenzopyrylium chloride* gave with sodium acetate a red *base* (V) which could be crystallised (although with difficulty) from its solution in benzene. A study of its properties showed that it was a normal example of a base of the anhydronium type. Thus it formed, when heated with methyl sulphate, a salt of 7-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium hydroxide*, which was identified by direct comparison of the corresponding *ferrichloride* (VI) with an authentic specimen. A similar transformation of the anhydro-base by reaction with methyl iodide could not be effected, the failure being due in all probability to the insoluble nature of the base. The reaction with methyl sulphate renders the base directly comparable with the compound (VII) which was isolated in a crystalline condition by Armit and Robinson (J., 1925, **127**, 1604), and the discovery of this further example provides additional experimental evidence in support of the views of these authors regarding the structure of anhydronium bases.

Further evidence in support of the constitutional formulæ assigned to the orcylaldehyde monomethyl ethers has been obtained by connecting the present series of experiments with the work of Fischer and Hoesch (*Annalen*, 1912, **391**, 347) on the partly methylated orsellinic acids. This was accomplished by preparing from orcylaldehyde 3-methyl ether the corresponding carbomethoxy-derivative, 5-*methylcarbonato-orcylaldehyde* 3-*methyl ether* (5-*methylcarbonato*-3-*methoxy*-o-*tolualdehyde*). This substance was oxidised in neutral solution by potassium permanganate to give 5-methylcarbonato-3-methoxy-*o*-toluic acid (5-methylcarbonato-orsellinic acid 3-methyl ether), which had been prepared directly from orsellinic acid by Fischer and Hoesch (*loc. cit.*).

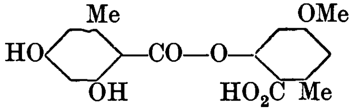
5-Methylcarbonato-orcylaldehyde 3-methyl ether is a phototropic substance, turning deep yellow when exposed to light for a few hours and becoming colourless again in the dark.

The action of alkali on 5-methylcarbonato-orsellinic acid 3-methyl ether led to the formation of orsellinic acid 3-methyl ether. The alternative formulæ suggested by Perkin and Everest ("The

Natural Organic Colouring Matters," 1918, pp. 549 and 551) for ramalic acid (one of the commoner lichen acids) require, in the form in which they are printed, that orsellinic acid 3-methyl ether should be one of the products formed on hydrolysis. But it was found by Hesse (*J. pr. Chem.*, 1898, **57**, 253; compare Perkin and Everest, *op. cit.*) that everninic acid and not orsellinic acid 3-methyl ether is obtained when ramalic acid is hydrolysed. In view of Fischer's work on evernic acid (*Ber.*, 1913, **46**, 3253; 1914, **47**, 505), which fixes its structure by relating it to lecanoric acid (Fischer and Fischer, *Ber.*, 1913, **46**, 1138), the alternative formulæ possible for ramalic acid should therefore be (VIII) and (IX). Experiments are now in progress by means of which it is hoped to be able to make a decision between the two.



(VIII.)



(IX.)

EXPERIMENTAL.

Pyrylium Salts from Orcylaldehyde.—(a) Orcylaldehyde (2 g.; prepared from orcinol by Gattermann's method, *loc. cit.*) and acetophenone (2 g.) were condensed in methyl-alcoholic solution (10 c.c.) by saturating the cold mixture with dry hydrogen chloride. The crystalline precipitate that appeared after a few minutes (yield, almost quantitative) was washed with a little methyl alcohol and recrystallised from hot water containing a little hydrochloric acid, 7-*hydroxy*-2-*phenyl*-5-*methylbenzopyrylium chloride* being obtained in long, yellow needles, m. p. 206° (decomp.) after darkening at 170°. The *perchlorate* (orange, rectangular prisms, m. p. indefinite but below 245°), *iodide* (red, rectangular prisms, m. p. 225° decomp.), *mercurichloride* (golden needles, m. p. 229—230° decomp.), and *ferrichloride* (golden-brown needles, m. p. 147—148° decomp. Found: C, 44·0; H, 3·3. $C_{16}H_{13}O_2Cl_4Fe$ requires C, 44·1; H, 3·0%) were prepared from the chloride by the usual methods. The behaviour of all the salts was normal. The chloride showed no fluorescence in methyl alcohol, but gave an apple-green fluorescence with sulphuric acid.

The corresponding *anhydro-base* (V) was precipitated by sodium acetate from a hot solution of the chloride in water. It was obtained crystalline on very slow evaporation of its solution in benzene, as dark red needles, which sintered and melted with decomp. at 156—165° (Found: C, 81·4; H, 5·5. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%). The base was very slightly soluble in water and showed a slight fluorescence in methyl alcohol. Boiling hydrochloric acid regenerated the chloride (m. p. 206°). The dry base did not react with methyl iodide in boiling benzene. When, however, the base was heated for 2 hours at 120° with an excess of freshly distilled methyl sulphate, reaction ensued and on addition of a mixture of hot water and hydrochloric acid, saturated with ferric chloride, 7-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium ferrichloride* was precipitated. This crystallised from acetic acid in golden-yellow, rectangular plates or needles, m. p. 181° (decomp.), and was identified by direct comparison with an authentic specimen (see below) (Found: C, 45·5; H, 3·6. $C_{17}H_{15}O_2Cl_4Fe$ requires C, 45·4; H, 3·3%).

(b) Orcylaldehyde and acetylanisole gave in good yield, under conditions similar to the above, 7-*hydroxy*-4′-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride*. This was insoluble in dilute hydrochloric acid and crystallised from methyl alcohol–dilute hydrochloric acid in red needles, m. p. 242—243° (decomp.) after darkening at 225° (Found: C, 61·6; H, 5·7. $C_{17}H_{15}O_3Cl,1\frac{1}{2}H_2O$ requires C, 61·9; H, 5·5%). The *iodide* (microscopic, red prisms, m. p. 235—236° decomp.) was insoluble in all the solvents tried, whereas the *ferrichloride* (yellow needles or elongated plates, m. p. 149—150° decomp.) was much more readily soluble in acetic acid than the corresponding 7-hydroxy-2-phenyl-5-methylbenzopyrylium ferrichloride. The chloride fluoresced strongly in sulphuric acid and in methyl alcohol and weakly in water and in acetic acid.

Pyrylium Salts from Everninaldehyde (*Orcylaldehyde* 5-*Methyl Ether*).—Hoesch's orcylaldehyde monomethyl ether (everninaldehyde, *Ber.*, 1913, **46**, 886) (2 g.) was dissolved in methyl alcohol (10 c.c.) containing acetophenone (2 g.), and dry hydrogen chloride was passed into the cooled solution. A brown, crystalline precipitate (2·5 g.) separated after a few minutes. This was filtered off, washed with cold methyl alcohol, and recrystallised from hot dilute hydrochloric acid, thus giving needles, m. p. 173—174° (decomp.), of 7-*methoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride* containing $1\frac{1}{2}$ molecules of water of crystallisation (Found: C, 65·3; H, 6·05. $C_{17}H_{15}O_2Cl,1\frac{1}{2}H_2O$ requires C, 65·1; H, 5·8%). The *iodide* (red, microscopic needles, m. p. 191—192° decomp.) and the ferrichloride (needles or rectangular plates from acetic acid; m. p. 181—182° decomp., after softening at 177°) were prepared in the usual way from the chloride. All the salts gave an intense apple-green fluorescence in water, methyl alcohol, or sulphuric acid.

Everninaldehyde, when condensed in a similar manner with acetylanisole, gave 4′ : 7-*dimethoxy*-2-*phenyl*-5-*methylbenzopyrylium chloride*, which crystallised from dilute hydrochloric acid in light red needles, m. p. 214—215° (decomp.) (Found: C, 62·9; H, 5·9. $C_{18}H_{17}O_3Cl,1\frac{1}{2}H_2O$ requires C, 62·8; H, 5·8%). The *ferrichloride* crystallised from acetic acid in yellow needles, m. p. 177° (decomp.). The chloride and the ferrichloride gave a very intense apple-green fluorescence in all solvents.

Condensation of Orcylaldehyde 3-*Methyl Ether with Acetylanisole.*—When Gattermann's orcylaldehyde 3-methyl ether (m. p. 188°) (2 g.), acetylanisole (1·9 g.), and potassium hydroxide (2 g. in 3 c.c. of water) were heated on the water-bath for 3½ hours in methyl-alcoholic solution (20 c.c.), condensation occurred to give p-*anisyl* 4-*hydroxy*-2-*methoxy*-6-*methylstyryl ketone* (III). Addition of water then gave an oil (decomposition products) and from the decanted liquor, on cooling, crystals of the ketone separated in yellow needles, m. p. 194—195° (Found: C, 64·8; H, 6·5. $C_{18}H_{18}O_4,2H_2O$ requires C, 64·7; H, 6·6%). The action of hydriodic acid on this substance led to demethylation followed by condensation to a pyrylium salt which showed an intense green fluorescence in concentrated sulphuric acid.

5-*Methylcarbonato-orcylaldehyde* 3-*Methyl Ether.*—Orcylaldehyde 3-methyl ether (5 g.) was dissolved in 50 c.c. of acetone and treated with methyl chloroformate (4 c.c.). The solution was cooled in ice and shaken vigorously during the addition of 60 c.c. of *N*-sodium hydroxide. An oil separated which was washed several times with cold water and soon solidified. This material crystallised from dilute acetone in long, colourless, phototropic needles, m. p. 80—81° (Found: C, 58·8; H, 5·2. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%).

5-Methylcarbonato-orcylaldehyde 3-methyl ether (5 g.) dissolved in acetone (25 c.c.) was treated gradually with a solution of potassium permanganate (6 g. in 100 c.c. of water containing 5 g. of crystallised magnesium sulphate), the temperature being maintained at 45°. The precipitated oxides of manganese were then removed by means of sulphur dioxide in the usual way. A quantity of oil separated from the clear solution, followed by a slow crystallisation of 5-methylcarbonato-orsellinic acid 3-methyl ether. Recrystallisation from ligroin–ethyl acetate gave the pure compound in colourless needles, m. p. 144° (yield, 2 g.). This substance yielded orsellinic acid 3-methyl ether when hydrolysed by Fischer and Hoesch's method (*loc. cit.*).

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[*Received, August 29th,* 1927.]