XXXIV.—*The Migration of the Acyl Group in Partly Acylated Phenolic Compounds. Part I.*

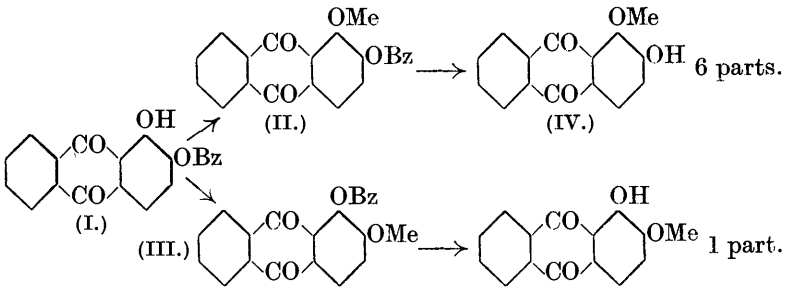
By ARTHUR GEORGE PERKIN and RALPH CHARLES STOREY.

WHEN 2-acetylalizarin is methylated with diazomethane (Kubota and Perkin, J., 1925, **127**, 1889) a wandering of the acetyl group occurs, 1-acetylalizarin 2-methyl ether (6 parts) and 2-acetylalizarin 1-methyl ether (1 part) being obtained. In an analogous manner, 2 : 3-diacetylanthragallol (referred to later) gives 1 : 3-diacetylanthragallol 2-methyl ether and 2 : 3-diacetylanthragallol 1-methyl ether, the former as chief product. When, however, 3 : 7 : 3′ : 4′-tetra-acetylquercetin is treated similarly, migration of the acetyl group does not occur, only 3 : 7 : 3′ : 4′-tetra-acetylquercetin 5-methyl ether being produced. The present investigation was undertaken to study, not only the behaviour of other partly acetylated hydroxy-ketones with diazomethane, but also the effect in these circumstances of the carbethoxy-, benzoyl, and toluene-*p*-sulphonyl groups. It was desirable again to devise a method whereby α-methyl ethers of the hydroxyanthraquinones, only traces of which have been hitherto available, could be obtained in reasonable amount for further study.

The general methods here devised for the preparation of the hitherto unknown partly acylated compounds required for this work, which are described in the sequel, hardly require comment. For the preparation of 2-benzoylalizarin and 2-benzoylanthrapurpurin, however, somewhat novel processes, involving the action of benzoyl chloride in presence of pyridine on 2-acetylalizarin and

2 : 7-diacetylanthrapurpurin, respectively, were employed. In the former case, 1-acetyl-2-benzoylalizarin, and in the latter 2-benzoyl-1 : 7-diacetylanthrapurpurin, was obtained, a migration of an acetyl group from the 1- to the 2-position having occurred in both cases. From these compounds by acid hydrolysis the desired 2-benzoylalizarin and 2-benzoylanthrapurpurin were obtained. Again, 2 : 3-diacetylanthragallol with excess of benzoyl chloride yielded the 2 : 3-dibenzoyl-1-acetyl compound (a reaction which involves the migration of one acetyl group and the replacement of a second by a benzoyl group); this by removal of the acetyl group gave the dibenzoylanthragallol required for investigation. In these cases, migration occurs during the benzoylation, and no alteration of the position of the benzoyl group occurs during the subsequent hydrolysis of the benzoylacetyl compound. These results thus differ from those observed by Fischer, Bergmann, and Lipschitz (*Ber.*, 1918, **51**, 45), who cite, together with other cases, the formation by hydrolysis of 3-benzoylgallic acid from 4-benzoyl-3 : 5-diacetylgallic acid and of 3-benzoylprotocatechuic acid from 4-benzoyl-3-acetyl-protocatechuic acid.

In the methylation, various solvents—ether, acetone, tetrachloroethane, and nitrobenzene—were employed, dependent in each case on the more ready solubility of the acetyl compound therein. From isolated experiments, it did not appear that the migration varied appreciably in amount by the use of one or other of these solvents, or that this could be rendered complete, or was indeed affected, by the employment of a very large amount of diazomethane. Owing to the formation of viscid matter, the yield of crystalline methylation product which could be isolated varied according to the acyl compound under investigation, and in some cases (compare acetylpurpurin) was poor. The results given below, expressed in parts, are the relative quantities of the methyl ethers isolated from the reaction product. 2-Benzoylalizarin (I), for



instance, gave preferably in tetrachloroethane 2-benzoylalizarin 1-methyl ether (II) (6 parts) and 1-benzoylalizarin 2-methyl ether

(III) (1 part). From these compounds by hydrolysis, alizarin 1- (IV) and 2-methyl ethers were respectively obtained.

In the other results, expressed as follows, the presence of an asterisk indicates that the compound though present was not isolated.

2-Ethylcarbonatoalizarin	1-Ethylcarbonatoalizarin 2-methyl ether	Alizarin 2-methyl ether (1 part)
	2-Ethylcarbonatoalizarin 1-methyl ether	Alizarin 1-methyl ether (3 parts)
2-Toluene-*p*-sulphonylalizarin	2-Toluene-*p*-sulphonylalizarin 1-methyl ether	Alizarin 1-methyl ether (sole product)
2 : 7-Diacetylanthrapurpurin	1 : 7-Diacetylanthrapurpurin 2-methyl ether *	Anthrapurpurin 2-methyl ether
	2 : 7-Diacetylanthrapurpurin 1-methyl ether *	Anthrapurpurin 1-methyl ether
2 : 7-Diethylcarbonatoanthrapurpurin	1 : 7-Diethylcarbonatoanthrapurpurin 2-methyl ether *	Anthrapurpurin 2-methyl ether (2 parts)
	2 : 7-Diethylcarbonatoanthrapurpurin 1-methyl ether	Anthrapurpurin 1-methyl ether (5 parts)
2-Benzoylanthrapurpurin	1-Benzoylanthrapurpurin 2 : 7-dimethyl ether	Anthrapurpurin 2 : 7-dimethyl ether
	2-Benzoylanthrapurpurin 1 : 7-dimethyl ether	Anthrapurpurin 1 : 7-dimethyl ether
2-Acetylpurpurin	1-Acetylpurpurin 2 : 4-dimethyl ether	Purpurin 1 : 3-dimethyl ether (5 parts)
	1-Acetylpurpurin 2-methyl ether	Purpurin 2-methyl ether (1 part)
2-Acetylpurpuroxanthin	3-Acetylpurpuroxanthin 1-methyl ether	Purpuroxanthin 1-methyl ether (sole product)
1 : 2(or 2 : 3)-Diethylcarbonatoanthragallol	2 : 3(or 1 : 2)-Diethylcarbonatoanthragallol 2-methyl ether	Anthragallol 1- or 3-methyl ether
	1 : 3-Diethylcarbonatoanthragallol 2-methyl ether	Anthragallol 2-methyl ether
3 : 4(or 2 : 3)-Diacetylgallacetophenone	2 : 4-Diacetylgallacetophenone 3-methyl ether	Gallacetophenone 3-methyl ether (A)
	3 : 4(or 2 : 3)-Diacetylgallacetophenone 2 (or 4)-methyl ether	Gallacetophenone 2 (or 4)-methyl ether (B)
3 : 4(or 2 : 3)-Ditoluene-*p*-sulphonylgallacetophenone	3 : 4(or 2 : 3)-Ditoluene-*p*-sulphonyl gallacetophenone 2 (or 4)-methyl ether	Gallacetophenone 2 (or 4)-methyl ether

In the above experiment with 2-acetylpurpurin, much viscid matter was produced, and therefore it is possible that traces of

2-acetylpurpurin 1-methyl ether were also present, but escaped detection.

The position of the methoxy-groups in these compounds could be deduced from their behaviour with boiling acetic anhydride; for instance, under identical conditions anthrapurpurin 1- and 2-methyl ethers yielded the 2 : 7- and 7-acetyl derivatives, respectively.

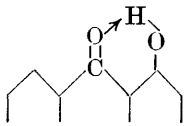
That the gallacetophenone methyl ether (A), which is identical with that obtained by one of us (J., 1903, **83**, 131) from monopotassium gallacetophenone and methyl iodide, contains the methoxy-group in position 3 is evident from its properties and the fact that (by methods described later) it yields pyrogallol 2-methyl ether. (B), on the other hand, which in similar circumstances gives pyrogallol 1-methyl ether, is either the 2- or 4-methyl ether of gallacetophenone, for although analogy suggests that it has the former constitution and that the partly acetylated gallacetophenone from which it is derived is the 3 : 4-acetyl compound, this is hardly certain, because in view of the work of Pascu (*Ber.*, 1923, **56**, 407) on the acetyl derivatives of 2 : 3 : 4-trihydroxybenzoic acid, a possibility exists that this may be the 2 : 3-diacetyl derivative. A similar uncertainty exists in regard to the position of the acetyl groups in the partial acetylation product of anthragallol, which by analogy with alizarin has been hitherto assumed to be the 2 : 3-diacetyl derivative, for there is a possibility as a result of the work of one of us and Mr. C. W. H. Story now in progress, that the acetyl groups may be in the 1 : 2-diacetyl positions and that the product of its methylation, described by Kubota and Perkin (*loc. cit.*) as anthragallol 1-methyl ether, is in reality the 3-methoxy-compound.

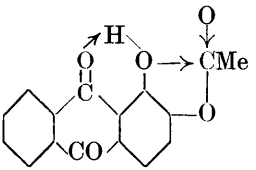
The results of this and the preceding investigation (*loc. cit.*) show that by methylating the hydroxyacetoxyanthraquinones enumerated above with diazomethane the migration of the acetyl group approximates to 85%. When the ethylcarbonato-group is similarly present, this wanders to a less extent (about 25%), and the migration of the benzoyl group is even smaller (about 20%). With the toluene-*p*-sulphonyl group, however, migration does not occur, and as a result a method is now available whereby good yields of the 1 (or 3)-methyl ethers of hydroxyanthraquinones or hydroxyketones can be obtained.

When, as with monoacetylpurpuroxanthin, the acetoxy- and hydroxy-groups are not vicinal, migration of the acetyl group does not occur under the influence of diazomethane, as was also the case with 4 : 7 : 3′ : 4′-tetra-acetylquercetin in similar circumstances (*loc. cit.*). Somewhat analogous are the results of Bergmann and Dangschat (*Ber.*, 1919, **52**, 371), who observed that the migration

of the benzoyl group described by Fischer, Bergmann, and Lipschitz, referred to above, does not take place with similar derivatives of β-resorcylic and gentisic acids. Again, migration of the benzoyl group does not occur when 2-benzoylresorcylic acid is submitted to the action of diazomethane.

Adopting the suggestion of Sidgwick and Callow (J., 1924, **125**, 527; compare Dimroth and Faust, *Ber.*, 1921, **54**, 3126) that the inert character of the α-hydroxyl of hydroxy-ketones in comparison with that in the β-position is to be explained by the presence of a six-membered chelate ring (V), it would appear that, if in such

(V.) 

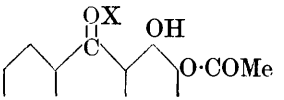
 (VI.)

compounds the attraction of the carbonyl for the 1-hydroxyl was removed, the latter would then possess more " basic " properties, or a greater attraction for the acyl group, than that in the 2-position. Such a view receives some support from the work of Bergmann and Dangschat (*loc. cit.*), who showed that by cautious hydrolysis both diacetyl-β-resorcylic acid and diacetylgentisic acid yielded the 2-acetyl derivative. Again (Pascu, *loc. cit.*), by similar treatment, 4-hydroxy-2 : 3-diacetoxybenzoic acid gives apparently the 3 : 4-dihydroxy-2-acetoxy-compound.

That, on the other hand, the 2-hydroxyl of the hydroxy-ketone dyes has marked " acidic " property is suggested by the fact (Perkin, J., 1899, **75**, 433) that by the action of alcoholic potash, or alcoholic potassium acetate, on these compounds the 2-potassiumoxy-salt is first produced. The 2-hydroxyl is, however, more readily acylated than the 1-hydroxyl, and this apparent anomaly may be due to the fact that the " basic " function of the latter is suppressed, at least in part, by its co-ordination with the carbonyl group. It seems likely that the 2-acetyl group to some extent attracts the 1-hydroxyl, so that the chelate ring is weakened—an effect which may be expressed (VI) by means of a co-ordinate link between the oxygen of the 1-hydroxyl and the acetyl group.

In discussing the migration of the acyl group from the 2- to the 1-position under the influence of diazomethane, the transformation of 2-acetylalizarin into 1-acetylalizarin 2-methyl ether may be taken as typical. Although a trace of 2-acetylalizarin 1-methyl ether is present in the reaction product, there is no reason to presume that this is the initial product of the reaction, from which, by an interchange in the positions of methyl and acetyl, the 1-acetyl-

alizarin 2-methyl ether is formed subsequently. It seems more probable indeed that migration of the acetyl from the 2- to the 1-position first occurs, and that this is followed by the methylation of the 2-hydroxyl thus vacated. For these changes to occur, it is probable that, as a preliminary, the influence of the carbonyl on the 1-hydroxyl has been suppressed or rendered non-existent, and that this, it is suggested, may have arisen from the production of a loose compound of diazomethane with the carbonyl oxygen. The nature of such a combination need not be at present discussed and is here (VII) referred to as X.



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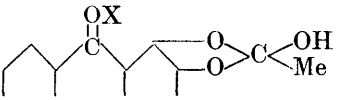
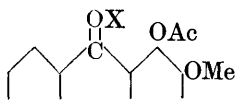
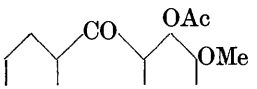


(VIII.)

As a result, the full attraction of the 1-hydroxyl for the acetyl group now comes into play, and migration of the latter from the 2- to the 1-position occurs, possibly *via* some intermediate stage as (VIII), a type of change which has been suggested by Fischer, Bergmann, and Lipschitz (*loc. cit.*) in explanation of the wandering of the benzoyl group in the benzoylhydroxybenzoic acids above referred to. Excess of diazomethane being present, methylation of the 2-hydroxyl (IX) now occurs, and finally, as diazomethane disappears from the solution, the addition product of the latter with the carbonyl group suffers decomposition (X).

(IX.) 



(X.)

Should the co-ordinating effect of the carbonyl be concerned with the para- rather than with the α-hydroxyl, as may perhaps be the case in the diacetylanthragallol and diacylgallacetophenones here studied, then the migration of the acyl group which occurs when these compounds are treated with diazomethane can be similarly explained.

Such a theory will also account for the wandering of the acetyl group during benzoylation, as in the formation of 2-benzoyl 1-acetylalizarin from 2-acetylalizarin (*loc. cit.*), it being assumed, in this case, that the formation of a loose compound between the carbonyl and either benzoyl chloride or the catalyst precedes the migration process.

The fact that in similar circumstances the ethylcarbonato- and benzoyl groups wander to a less extent than the acetyl group is probably to be accounted for by their higher molecular weight and

lower acidity, and consequent resistance to displacement, whereas the complete lack of migration shown by the strongly acid toluene-*p*-sulphonyl radical can only be explained on the former assumption.

An account of the preparations, from anthragallol, of the anthragallol 1 : 3- and 1 : 2-dimethyl ethers present in Chay Root which has been recently effected by one of us and Mr. C. W. H. Story will be communicated to the Society in due course.

EXPERIMENTAL.

2 : 7-*Diacetylanthrapurpurin*—Commercial anthrapurpurin purified by the method of Goodall and Perkin (J., 1924, **125**, 473) (5 g.) was digested with a boiling mixture of acetic anhydride (50 c.c.) and acetic acid (50 c.c.). Twenty drops of pyridine were added, and when solution was complete the liquid was poured into alcohol. The deposit, recrystallised from alcohol–acetic acid, gave fine, yellow needles, m. p. 192—193° (Found : C, 63·3 ; H, 3·6. $C_{18}H_{12}O_7$ requires C, 63·5 ; H, 3·55%).

Alternatively, potassium acetate (2·5 g.) was boiled with acetic anhydride (25 c.c.) and, when the mixture was cold, anthrapurpurin (5 g.) was added. The crystals which had separated over-night melted at 192—193° after recrystallisation. The diacetyl compound which is described by Knoll and Co. (D.R.-P. 117730) as melting at 175—178°, and is said to be prepared by the gentle acetylation of anthrapurpurin, can hardly be a pure compound.

Methylation. 2 : 3-Diacetylanthrapurpurin (2 g.) in nitrobenzene (35 c.c.) or acetone (150 c.c.) was treated with ethereal diazomethane from nitrosomethylurethane (9·25 c.c.). After 2 days, the filtered solution was freed from ether and steam-distilled to remove nitrobenzene. The viscid residue was hydrolysed in acetic acid (15 c.c.) with hydrochloric acid in the usual manner, and hot water cautiously added to the solution. When cold, the crystals were collected and fractionally crystallised from alcohol. The sparingly soluble fraction, which formed orange-red needles, m. p. 308—309°, consisted of *anthrapurpurin 2-methyl ether* (Found : C, 66·7 ; H, 4·1 ; CH_3, 5·6. $C_{15}H_{10}O_5$ requires C, 66·7 ; H, 3·7 ; CH_3, 5·55%).

1 : 7-*Diacetylanthrapurpurin 2-methyl ether*, obtained by means of acetic anhydride and pyridine, crystallises in yellow leaflets, m. p. 154—155° (Found : C, 64·1 ; H, 4·0. $C_{19}H_{14}O_7$ requires C, 64·4 ; H, 4·0%). By a short digestion, however, with boiling acetic anhydride in the absence of pyridine, orange-yellow needles, m. p. 207°, of *7-acetylanthrapurpurin 2-methyl ether* are obtained.

The alcoholic mother-liquor from which the 2-methyl ether had separated was treated with baryta water, to precipitate as barium

salt traces of the latter still present; the mixture was then boiled and filtered, and the filtrate made acid with hydrochloric acid. The crystals which separated were acetylated, for which purpose the use of pyridine was unnecessary, and the 2 : 7-*diacetylanthrapurpurin* 1-*methyl ether* recrystallised first from acetone and then from alcohol. It consisted of pale yellow leaflets, m. p. 136—137° (Found : C, 64·2; H, 3·95. $C_{19}H_{14}O_7$ requires C, 64·4; H, 4·0%).

Hydrolysis with hydrochloric acid gave orange-red needles of *anthrapurpurin* 1-*methyl ether*, m. p. 299—300° (Found : $C_{15}H_{10}O_5$, 76·2. Calc., 76·3%. Found : C, 67·0; H, 4·0; CH_3, 5·3. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7; CH_3, 5·5%).

2 : 7-*Diethylcarbonatoanthrapurpurin*.—Anthrapurpurin (2 g.) in pyridine (25 c.c.) was treated drop by drop with ethyl chloroformate (1·8 c.c.), the temperature being kept at about 30°. After 1 hour, water (20 c.c.) was slowly added, and when crystals ceased to separate these were collected and recrystallised from alcohol. The golden-yellow needles melted at 166—167° (Found : C, 60·1; H, 4·25. $C_{20}H_{16}O_9$ requires C, 60·0; H, 4·0%). Yield, 1·43 g.

Methylation. 2 : 7-Diethylcarbonatoanthrapurpurin (2 g.) in tetrachloroethane (30 c.c.) was treated with diazomethane from nitrosomethylurethane (8 c.c.). After 3 days, the filtered solution was steam-distilled, and the viscid residue well dried. A solution of the latter in methyl alcohol (25 c.c.) (charcoal), deposited lemon-yellow needles of pure 2 : 7-*diethylcarbonatoanthrapurpurin* 1-*methyl ether* (0·75 g.), m. p. 120—121° (Found : C, 60·8; H, 4·2. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%).

For hydrolysis, boiling 1% methyl-alcoholic potash was used, and the claret solution was diluted with water and acidified with hydrochloric acid. The yellow needles of anthrapurpurin 1-methyl ether which separated (0·5 g.) melted at 299—300° (Found : C, 66·6; H, 3·8%).

The alcoholic mother-liquors from which the 2 : 7-diethylcarbonatoanthrapurpurin 1-methyl ether had separated were concentrated, and while boiling, treated with a little methyl-alcoholic potash. The diluted solution on acidification deposited orange needles of anthrapurpurin 2-methyl ether (0·2 g.), m. p. 308—309° (Found : C, 66·5; H, 4·1%).

2-*Benzoyl*-1 : 7-*diacetylanthrapurpurin*—To 2 : 3-diacetylanthrapurpurin (1 g.) in chloroform (6 c.c.) and benzoyl chloride (1·3 c.c.), pyridine (1 c.c.) was slowly added, rise of temperature being avoided. After 2 days, the mixture was diluted with alcohol, and the separated product recrystallised from alcohol or acetic acid. The pale yellow plates or leaflets melted at 201—203° (Found : C, 67·7; H, 3·8. $C_{25}H_{16}O_8$ requires C, 67·6; H, 3·6%).

2-*Benzoylanthrapurpurin.*—By cautious hydrolysis of the benzoyldiacetyl compound, 79·8% of 2-benzoylanthrapurpurin was obtained, (theoretical, 80·5%). The product crystallised from methyl alcohol or tetrachloroethane as yellow plates or prisms, m. p. 272—273° (Found : C, 69·85; H, 3·6. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3%). The yield reckoned on the diacetylanthrapurpurin employed was about 20%.

Methylation. A solution of 2-benzoylanthrapurpurin (2 g.) in hot tetrachloroethane (120 c.c.) was cooled, some crystals separating, and the mixture was treated with diazomethane from nitrosomethylurethane (14 c.c.). After 2 days, the filtered solution was steam-distilled, and the viscid residue dissolved in hot methyl alcohol (550 c.c.) (charcoal). The crystals of the sparingly soluble 2-*benzoylanthrapurpurin* 1 : 7-*dimethyl ether* (Filtrate A), by recrystallisation from methyl alcohol, formed lemon-yellow leaflets, m. p. 201—203° (Found : C, 71·1; H, 4·15; CH_3, 7·7. $C_{23}H_{16}O_6$ requires C, 71·1; H, 4·1; CH_3, 7·7%).

For hydrolysis, boiling 2% methyl-alcoholic potash was used, and the solution was diluted with hot water and acidified. Yellow needles of *anthrapurpurin* 1 : 7-*dimethyl ether*, m. p. 218—219°, soluble in dilute alkali with a red colour, thus separated (Found : C, 67·6; H, 4·3. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

Acetylation in the absence of pyridine yielded 2-*acetylanthrapurpurin* 1 : 7-*dimethyl ether* as pale yellow needles, m. p. 175—176°.

The methyl-alcoholic filtrate (A) on evaporation to about 50 c.c. gave crystals, which were deposited from alcohol–acetic acid as yellow plates, m. p. 209—211° (Found : C, 70·5; H, 4·1; CH_3, 7·9. $C_{23}H_{16}O_6$ requires C, 71·1; H, 4·1; CH_3, 7·7%). This compound, which is evidently 1-*benzoylanthrapurpurin* 2 : 7-*dimethyl ether*, by hydrolysis with methyl-alcoholic potash, yielded orange-yellow needles of anthrapurpurin 2 : 7-dimethyl ether, m. p. 242—243°, a substance which has been previously prepared by Graebe and Bernhard (*Annalen*, 1906, **349**, 222) (Found : C, 67·45; H, 4·4%). The barium salt of the 1 : 7-dimethyl ether is soluble in water, whereas that of the 2 : 7-dimethyl ether is insoluble. Acetylation gave 1-acetylanthrapurpurin 2 : 7-dimethyl ether as pale yellow needles, m. p. 228—230°.

Purpurin.—Commercial purpurin was extracted with boiling (purified) solvent naphtha. The crystals which separated from the extract on cooling were employed without further purification.

2-*Acetylpurpurin.* To a well-stirred mixture of potassium acetate (1 g.) and cold acetic anhydride (10 c.c.) purpurin (2 g.) was added. After being kept over-night, the product was collected and recrystallised from alcohol, forming orange needles, m. p. 179—

180°. Alternatively, purpurin (10 g.) in pyridine (100 c.c.) was treated gradually with acetic anhydride (4 c.c.) and after 1 hour water was slowly added. The deposit was recrystallised from alcohol (Found : C, 64·2; H, 3·5. $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·35%). Hydrolysis gave 85·5% of purpurin (Calc., 85·9%).

Methylation. 2-Acetylpurpurin (2 g.) in tetrachloroethane (30 c.c.) (ether and acetone also were employed as solvents) was treated with diazomethane from nitrosomethylurethane (10 c.c.). After 2 days, the solution was steam-distilled, the viscid product dried as completely as possible and extracted with ether (insoluble residue A), the extract evaporated, and the residue crystallised from alcohol (yield, 0·15 g.) (Found : C, 66·35; H, 4·5; CH_3, 9·0. $C_{18}H_{14}O_6$ requires C, 66·1; H, 4·3; CH_3, 9·2%).

1-*Acetylpurpurin* 2 : 4-*dimethyl ether* forms lemon-yellow needles, m. p. 189—190°, and when hydrolysed with hydrochloric acid in the usual manner, gives fine, orange needles of *purpurin* 2 : 4-*dimethyl ether*, m. p. 186—189° (Found : C, 67·55; H, 4·0. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

The residue (A) undissolved by the ether was extracted with boiling acetone, and the crystals deposited from the extract were recrystallised from acetone. 1-*Acetylpurpurin* 2-*methyl ether* was thus obtained as yellow needles, m. p. 224—225° (Found : C, 65·5; H, 3·8. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·8%). Acetylation employing pyridine gave yellow needles of 1 : 4-*diacetylpurpurin* 2-*methyl ether*, m. p. 170—172°, and by hydrolysis with hydrochloric acid, fine, brick-red needles of purpurin 2-monomethyl ether, m. p. 232—233°, soluble in alkalis with a crimson coloration, were obtained (Found : C, 66·6; H, 3·6; CH_3, 5·5. Calc. for $C_{15}H_{10}O_5$: C, 66·7; H, 3·7; CH_3, 5·5%). It is identical with the methyl ether, described as melting at 228—230°, obtained by Perkin (*loc. cit.*) from monopotassium purpurin and methyl iodide.

Purpuroxanthin.—For the preparation of this compound, purified purpurin (*loc. cit.*) was reduced with sodium hydrosulphite. Before crystallisation the elimination of sulphur with carbon disulphide was necessary.

3-*Acetylpurpuroxanthin* was prepared from potassium acetate (2·5 g.), acetic anhydride (15 c.c.), and purpuroxanthin (5 g.) in the cold (see purpurin). The product crystallised from alcohol (charcoal) as long, yellow needles, m. p. 144° (Found : C, 68·0; H, 3·6. $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·5%).

Methylation. 3-Acetylpurpuroxanthin (2 g.), tetrachloroethane (40 c.c.), and nitrosomethylurethane (8 c.c.) were employed. After 3 days, the product was distilled with steam and the well-dried tarry residue dissolved in boiling alcohol (60 c.c.) (charcoal). An

amorphous precipitate separated (Filtrate A) which by crystallisation from the same solvent formed lemon-yellow leaflets (0·78 g.) of 3-*acetylpurpuroxanthin* 1-*methyl ether*, m. p. 154—155° (Found: C, 68·8; H, 4·2; CH_3, 5·3. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0; CH_3, 5·0%). Hydrolysis with hydrochloric acid gave *purpuroxanthin* 1-*methyl ether*, which separated from acetone as yellow leaflets, m. p. 311—313° (Found: C, 71·1; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·8; H, 3·9%). The high melting point of this compound, compared with that of the 3-methyl ether, which melts at 193° (Graebe and Bernhard, *loc. cit.*), suggested that this compound was in reality a methylpurpuroxanthin methyl ether, formed by the entry of a methyl group into the ring during methylation. This, however, was not the case, as demethylation with fuming hydrochloric acid at 180° yielded purpuroxanthin, identified as diacetylpurpuroxanthin, m. p. 178—181°. The presence of a second acetylpurpuroxanthin methyl ether in filtrate (A) could not be detected.

Alizarin.—2-Benzoylalizarin. (*a*) 2-Acetylalizarin (3 g.) in chloroform (15 c.c.) and benzoyl chloride (3 g.) was slowly treated with pyridine (3 c.c.). Crystals of 2-*benzoyl*-1-*acetylalizarin* gradually separated, and the amount was increased by the addition of alcohol to the mixture (yield, 3 g.). Recrystallisation from acetone gave yellow needles, m. p. 172—174° (Found: C, 71·4; H, 3·6. $C_{23}H_{14}O_6$ requires C, 71·5; H, 3·6%). Hydrolysis was effected by employing hydrochloric acid (5 c.c.) in acetic acid (30 c.c.) at 100° for 3 hours, the 2-benzoylalizarin thus obtained separating from its solution in pyridine as long, orange-yellow needles, m. p. 220—221° (Found: C, 73·1; H, 3·6. $C_{21}H_{12}O_5$ requires C, 73·2; H, 3·5%).

(*b*) 2-Potassioalizarin (from 2-acetylalizarin and alcoholic potassium acetate), suspended in chloroform, was treated with benzoyl chloride. After keeping, the orange-yellow crystals were collected, washed with dilute ammonia to remove traces of alizarin, and recrystallised from pyridine. The product melted at 220—221° and was identical with the benzoylalizarin obtained by method (*a*), which is consequently the 2-benzoyl compound. Acetylation gave the 2-benzoyl-1-acetylalizarin described above, indicating that migration of the benzoyl group does not occur when the latter compound is hydrolysed.

Methylation. 2-Benzoylalizarin (2 g.), tetrachloroethane (30 c.c.), and nitrosomethylurethane (8 c.c.) were employed, and after 2 days the crystalline deposit (0·35 g.) was collected (Filtrate A) and recrystallised from much benzene. 1-*Benzoylalizarin* 2-*methyl ether* thus separated as a pale yellow, crystalline powder, m. p. 266—

268° (Found : C, 73·7; H, 3·8. $C_{22}H_{14}O_5$ requires C, 73·4; H, 3·95%). Hydrolysis with 1% alcoholic potash gave a red solution which on dilution with water and acidification deposited orange-red needles of alizarin 2-methyl ether, m. p. 228—230°, from which the acetyl derivative, m. p. 204—206°, was prepared. 1-Benzoylalizarin 2-methyl ether can be readily prepared from alizarin 2-methyl ether (1 g.), chloroform (60 c.c.), and benzoyl chloride (1 c.c.), pyridine (1 c.c.) being gradually added. The pale orange crystals were collected and washed with alcohol (1·25 g.). They had the properties described above.

The mother-liquor (A) was steamed-distilled and the residue fractionally crystallised from benzene to remove a trace of 1-benzoylalizarin 2-methyl ether. The main and more soluble fraction, consisting of 2-benzoylalizarin 1-methyl ether (0·8 g.), was isolated as yellow prisms, m. p. 203—205° (Found : C, 73·4; H, 4·0. $C_{22}H_{14}O_5$ requires C, 73·4; H, 3·95%). Hydrolysis with 1% methyl-alcoholic potash (as with the previously described compound) gave hair-like needles of alizarin 1-methyl ether, m. p. 175—177° (Found : C, 70·7; H, 4·1%), the acetyl derivative of which melted at 211—212°. The main product of the methylation of 2-benzoylalizarin is thus 2-benzoylalizarin 1-methyl ether.

Diethylcarbonatoalizarin was prepared from alizarin (1 g.), chloroform (6 c.c.), ethyl chloroformate (2 g.), and pyridine (2 c.c.), the mixture being kept for 2 days. The product (1 g.), recrystallised from alcohol, formed yellow needles, m. p. 150—157° (Found : C, 62·5; H, 4·3. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%).

2-*Ethylcarbonatoalizarin.* Commercial alizarin (5 g.) in pyridine (50 c.c.) was treated with ethyl chloroformate (2·1 g.) and after 30 minutes water was slowly added, the mixture being well shaken. The product (4·6 g.), recrystallised first from alcohol and then from acetone, consisted of flat, yellow needles, m. p. 138—140° (Found : C, 65·5; H, 4·0. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·85%).

Methylation. 2-Ethylcarbonatoalizarin (2 g.) in ether (50 c.c.) was treated with diazomethane from nitrosomethylurethane (8 c.c.), and the mixture kept for 2 days. The long, yellow needles (1·2 g.) were collected (A) and the filtrate was evaporated to dryness. By trituration with alcohol the viscid residue gave crystals (0·4 g.) (B). From (A) by recrystallisation from small amounts of benzene, almost colourless plates or prisms, m. p. 213—215°, were obtained (Found : C, 66·7; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). This compound, 1-*ethylcarbonatoalizarin* 2-*methyl ether*, by hydrolysis with alcoholic potash gave alizarin 2-methyl ether.

The benzene filtrates (A) were evaporated to dryness, the residue was added to (B), and the mixture fractionally crystallised from

alcohol. The main and more soluble fraction formed yellow needles, m. p. 145—147° (Found : C, 66·1; H, 4·45%), evidently 2-*ethylcarbonatoalizarin* 1-*methyl ether*, from which, by hydrolysis in the usual manner, hair-like needles of alizarin 1-methyl ether were obtained (Found : C, 68·8; H, 4·2%).

To determine whether the migration of the acyl group (in this case the ethylcarbonato-group) is influenced by the amount of diazomethane used in the methylation process, the foregoing experiment (I) was repeated, and a second (II), employing 12 c.c. of nitrosomethylurethane, simultaneously carried out, the conditions being identical in each case. The crystalline deposit (compare A above) from Experiment I gave by fractional crystallisation from benzene 0·44 g. of 1-ethylcarbonatoalizarin 2-methyl ether, and the residue obtained by the evaporation of the combined mother-liquors yielded on hydrolysis 1·1 g. of crude alizarin 1-methyl ether, equivalent to 1·41 g. of 2-ethylcarbonatoalizarin 1-methyl ether. In Experiment II, 1-ethylcarbonatoalizarin 2-methyl ether (0·45 g.) and crude alizarin methyl ether (1·11 g.) equivalent to 2-ethylcarbonatoalizarin 1-methyl ether (1·42 g.) were obtained. As by acetylation the crude alizarin 1-methyl ether from (I) gave 0·88 g., and that from (II) 0·86 g., of pure acetyl compound, m. p. 211—213°, it appears evident that the migration of the acyl group is not materially affected by an increase in the concentration of the diazomethane present.

2-*Toluene*-p-*sulphonylalizarin*. To a well-cooled mixture of alizarin (0·5 g.) and toluene-*p*-sulphonyl chloride (0·8 g.) in chloroform (3 c.c.) pyridine (0·8 c.c.) was gradually added. After 1 hour, dilution with alcohol caused the separation of orange-yellow plates, which were recrystallised from alcohol and acetic acid; they then melted at 218—219° (Found : C, 64·0; H, 3·6; S, 8·2. $C_{21}H_{14}O_6S$ requires C, 64·0; H, 3·55; S, 8·1%).

Methylation. A solution of 2-toluene-*p*-sulphonylalizarin (2 g.) in warm tetrachloroethane, cautiously cooled to avoid the separation of crystals, was at once treated with diazomethane (nitrosomethylurethane, 8 c.c.) and kept for 2 days. Steam distillation gave a crystalline residue which after recrystallisation from acetic acid–methyl alcohol melted at 176—177° (yield, 1·5 g.) (Found : C, 64·5; H, 4·1. $C_{22}H_{16}O_6S$ requires C, 64·7; H, 3·9%). The hydrolysis of this compound with boiling 2% methyl-alcoholic potash could only be gradually effected, the claret-red liquid being decanted from time to time, and the unattacked residue treated with fresh amounts of reagent until all had passed into solution. For 0·5 g. of substance 200 c.c. of the alcoholic potash were employed. The alkaline solution, diluted with water, acidified,

and boiled to expel alcohol, gave needles of alizarin 1-methyl ether, m. p. 181—182° (Found: C, 70·8; H, 4·1%). The alcoholic–acetic acid mother-liquors when evaporated to dryness gave a residue from which, by hydrolysis, only alizarin 1-methyl ether was obtained. It is thus evident that in these circumstances a migration of the toluene-*p*-sulphonyl group does not occur.

Anthragallol.—2 : 3-*Diethylcarbonatoanthragallol.* To anthragallol (2 g.) in pyridine (20 c.c.), ethyl chloroformate (2·6 c.c.) was gradually added and the mixture kept for 30 minutes. On addition of water (20 c.c.) and thorough shaking, crystals (1·9 g.) separated, which were recrystallised first from benzene (charcoal) and then from acetone. The orange-coloured prisms melted at 174—175° (Found: C, 60·9; H, 4·1. $C_{20}H_{16}O_9$ requires C, 60·0; H, 4·0%).

Methylation. 2 : 3-Diethylcarbonatoanthragallol (4 g.) was treated with diazomethane as described under diethylcarbonatoanthrapurpurin, and the product steam-distilled. A solution of the residue in boiling alcohol containing acetone gave crystals which by recrystallisation from acetone were obtained as large, yellow prisms, m. p. 125—127°. The yield of this compound, possibly 2 : 3- or 1 : 2-*diethylcarbonatoanthragallol* 1-(or 3)*methyl ether*, was 3·13 g. (Found: C, 60·7; H, 4·1. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%). From the acetone mother-liquors a product was isolated which after fractional crystallisation from alcohol formed pale yellow needles (0·12 g.), m. p. 196—197°, which apparently consisted of 1 : 3-*diethylcarbonatoanthragallol* 2-*methyl ether* (Found: C, 60·9; H, 4·6%). These products will be further examined.

Gallacetophenone.—The commercial product Alizarine Yellow C was recrystallised from water (charcoal) until of constant melting point.

Diacetylgallacetophenone. Gallacetophenone (5 g.) in cold acetic acid (15 c.c.) and acetic anhydride (7 c.c.) was treated with pyridine (2 c.c.), drop by drop, and kept for 18 hours. The solution was then poured into water (400 c.c.), and the precipitate collected, dried on tile, and crystallised from alcohol. The long, colourless needles melted at 107—108° (Found: C, 57·2; H, 4·9; Ac, 34·15. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8; Ac, 34·1%).

Methylation. Diacetylgallacetophenone (2 g.), tetrachloroethane (10 c.c.), and nitrosomethylurethane (8 c.c.) were employed. After 3 days, colourless plates (A) (0·96 g.) had separated which after recrystallisation from alcohol melted at 150—151° (Found: C, 58·7; H, 5·3; CH_3, 5·7. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3; CH_3, 5·5%). This compound, 2 : 4-*diacetylgallacetophenone* 3-*methyl ether* treated with boiling aqueous sodium carbonate, gave eventually a clear solution, from which, when neutralised, long needles of

gallacetophenone 3-methyl ether, m. p. 134—135°, separated (Found : C, 59·7; H, 5·4. Calc. for $C_9H_{10}O_4$: C, 59·3; H, 5·5%). As re-acetylation gave the acetyl compound melting at 150—151°, a migration of the methyl group does not occur during the subsequent hydrolysis of this compound. This substance, as already indicated, is identical with that, m. p. 132—133°, obtained from 2-potassiogallacetophenone by Perkin and Allen (*loc. cit.*), who gave the melting point of the acetyl derivative as 146—148°.

The tetrachloroethane filtrate from (A) was steam-distilled and the residual aqueous liquid, which deposited needles, m. p. 143—147°, was treated with boiling aqueous sodium carbonate to hydrolyse the acetyl compound present. The neutralised solution was evaporated to dryness, the residue extracted with boiling alcohol, and the solution clarified with charcoal and treated in the cold with alcoholic lead acetate. The lead salt of gallacetophenone 3-methyl ether thus precipitated (from which a further quantity of this 3-methyl ether was isolated) was removed, and the filtrate rendered faintly acid with sulphuric acid and evaporated to dryness. A concentrated methyl-alcoholic extract of the residue slowly deposited prisms of *gallacetophenone* 2- or 4-*methyl ether*, which after recrystallisation melted at 175° (Found : C, 59·1; H, 5·6%). Whereas gallacetophenone 2- or 4-methyl ether gives with alcoholic lead acetate a lead salt soluble in alcohol but insoluble in water, the lead compound of the 3-methyl ether is insoluble in alcohol and soluble in water.

Ditoluene-p-*sulphonylgallacetophenone*. A well-cooled mixture of gallacetophenone (1 g.), chloroform (6 c.c.), and toluene-*p*-sulphonyl chloride (4·6 g.) was slowly treated with pyridine (1·6 c.c.). After 1 hour, the product, diluted with alcohol (15 c.c.), was treated cautiously with water. The colourless plates (2·14 g.), thus obtained, recrystallised from methyl alcohol, melted at 152—153° (Found : C, 55·3; H, 4·3; S, 13·5. $C_{22}H_{20}O_8S_2$ requires C, 55·5; H, 4·2; S, 13·4%).

Methylation. This compound (2 g.), tetrachloroethane (15 c.c.), and nitrosomethylurethane (15 c.c.) were employed, the mixture being kept for 2 days. Distillation with steam yielded a pale yellow, oily residue, which was dried and dissolved in methyl alcohol (10—15 c.c.) (charcoal). On keeping, clusters of colourless needles (1·3 g.) of *ditoluene*-p-*sulphonylgallacetophenone* 2- or 4-*methyl ether*, m. p. 111—113°, separated (Filtrate A) (Found : C, 56·3; H, 4·6; CH_3, 3·1. $C_{23}H_{22}O_8S_2$ requires C, 56·3; H, 4·5; CH_3, 3·1%). Digestion with boiling 2% methyl-alcoholic potash, dilution with water, and neutralisation gave crystals of *gallacetophenone* 2- or 4-*methyl ether*, which, after recrystallisation from methyl alcohol, melted at 175° (Found : C, 59·2; H, 5·3%).

The methyl-alcoholic mother-liquor (A) was boiled with a little alcoholic potash for a short time to hydrolyse any ditoluene-*p*-sulphonyl compound present, and the solution acidified. Examination of the viscid mass revealed the absence of gallacetophenone 3-methyl ether and it was thus apparent that only ditoluene-*p*-sulphonylgallacetophenone 2- or 4-methyl ether is produced when ditoluene-*p*-sulphonylgallacetophenone is methylated with diazomethane.

Position of the Methoxy-group in the Gallacetophenone Methyl Ethers.—Gallacetophenone methyl ether (1 g.) melting at 150—151° was heated with alcoholic potash for 4 hours at 180° in a sealed tube. The solution, diluted with water and freed from alcohol by evaporation, was saturated with carbon dioxide and repeatedly extracted with ether to remove unattacked substance. From the acidified liquid, ether removed a viscid product, containing evidently a methyl ether of pyrogallolcarboxylic acid, and this was further purified by extraction with sodium bicarbonate in order to remove the last traces of gallacetophenone methyl ether. The product by dry distillation yielded a yellow oil, which gave a violet coloration with ferric chloride solution, an indication of the presence of pyrogallol 2-methyl ether. The acetyl compound crystallised from ligroin in colourless needles, m. p. 60—63°, and although according to Herzig and Pollak (*Monatsh.*, 1904, **25**, 808) 1 : 3-diacetylpyrogallol 2-methyl ether melts at 51—54°, there can be no doubt as to its identity with the compound produced as above stated from gallacetophenone 3-methyl ether. A similar experiment with the gallacetophenone methyl ether melting at 175° gave as final product a colourless oil, the acetyl compound of which melted at 87—89° (diacetylpyrogallol 1-methyl ether melts at 91—93°; *Monatsh.*, 1904, **25**, 501). As this crude methyl ether yielded an olive coloration with ferric chloride solution, it evidently contained pyrogallol 1-methyl ether, and this must have originated from either the 2- or the 4-methyl ether of gallacetophenone.

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CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, November 30th*, 1927.]