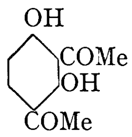
369. *A New Factor controlling Certain Chelations, with Special Reference to Disubstitution in the Resorcinol Nucleus.*

By Wilson Baker.

There are two known diacetylresorcinols, 2 : 4-diacetylresorcinol (I) and 4 : 6-diacetylresorcinol (II), the former having been prepared by Wittig, Baugert, and Richter (*Annalen*, 1925, **446**, 184) and by Rosenmund, Buchwald, and Deligiannis (*Arch. Pharm.*, 1933, **271**, 344; for the constitutions of these substances see Baker, this vol., p. 72). Both compounds contain two nuclear acetyl groups each adjacent to a hydroxyl group, so it might be expected that they should closely resemble each other, both physically and chemically, and that the same degree of chelation should be possible to both.



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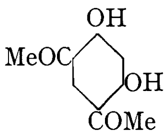

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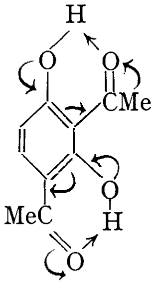

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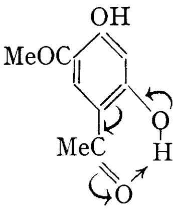

(IV.)

The two substances, however, exhibit pronounced differences in physical and in some chemical properties. 2 : 4-Diacetylresorcinol has m. p. 89° and b. p. 168—169°/10 mm.; it is soluble in 10 parts of benzene at 15°, easily soluble in light petroleum, and easily volatile in steam. 4 : 6-Diacetylresorcinol has m. p. 182°, b. p. 188—189°/10 mm., is soluble in 125 parts of benzene at 15°, almost insoluble in light petroleum, and almost non-volatile in steam. Stress must not be laid on the differences in melting point and solubility as an indication of chelation (see Sidgwick and Callow, J., 1924, **125**, 527), but as regards the boiling point it may be pointed out that resacetophenone has b. p. 179°/10 mm., so that introduction of the second acetyl group into resacetophenone in position 5 raises the boiling point by 10°, whilst in position 3 it lowers the boiling point by 10°.* It is difficult to avoid the conclusion that 2 : 4-diacetylresorcinol is considerably more chelated than the isomeric 4 : 6-diacetylresorcinol, which has the characteristics of a partially associated substance.

This is further borne out by the lowering of the melting points of the two substances under water. The melting point of 2 : 4-diacetylresorcinol is lowered by 5°, and that of 4 : 6-diacetylresorcinol by 23°, the small lowering in the first case being typical of certain highly chelated ortho-substituted phenols (see Sidgwick, Spurrell, and Davies, J., 1915, **107**, 1202). It has now been found, for example, that the melting point of the volatile 2-acetyl-*p*-cresol is lowered by only 1·5° under water, whilst the melting point of *p*-hydroxyacetophenone is lowered by 53°. Again, (I) with alcoholic ferric chloride produces a colour which is considerably deeper than that given by (II); and whilst (II), like resacetophenone, produces no visible dyeing on an iron mordant, 2 : 4-diacetylresorcinol gives a chocolate-brown dyeing.

There can be little doubt that these differences in behaviour are to be ascribed to the possible double chelation of 2 : 4-diacetylresorcinol (III), and the single chelation only of 4 : 6-diacetylresorcinol (IV), this in its turn depending on the necessity of the hydroxyl and the acetyl groups to be joined to mutually doubly linked carbon atoms of the benzene nucleus before chelation can occur. In (IV) the free hydroxyl group will cause the substance to be partially associated. No other reason for the differences between these diacetylresorcinols appears possible, and the explanation rests upon the reality of the Kekulé formula for benzene, evidence for which has been brought forward by Mills and Nixon (J., 1930, 2510), and provides evidence that the aromatic character of benzene is not dependent upon the rapid alternation of the double bonds. The difference between the diacetylresorcinols proves, quite independently of *any* theory, that in *o*-hydroxyacetophenone the bond uniting carbon atoms 3 and 4 differs from that uniting carbon atoms 4 and 5.

The view that a double bond between the carbon atoms bearing the hydroxyl and the acetyl group is a necessity for chelation receives support from a study of (*a*) certain aliphatic compounds and (*b*) orientation phenomena in resacetophenone derivatives.

(*a*) As an example, acetylacetone (largely enolic) has b. p. 137°; the corresponding saturated compound, 2-hydroxy-4-ketopentane, has b. p. 176—177°. Moreover the general properties of acetylacetone are those of a chelated compound, whilst 2-hydroxy-4-ketopentane possesses the solubilities, etc., of a hydroxylic substance.

(*b*) The preparation of 4 : 6-diacetylresorcinol (II) from resorcinol diacetate by heating with ferric chloride proceeds by two para-migrations of acetyl from oxygen to the nucleus, the intermediate 2-*O*-acetylresacetophenone (V) having been isolated by Gulati and Venkataraman (J., 1931, 2377). In this intermediate there is no factor fixing the double bonds in the nucleus, so the usually favoured para-migration of the second acetyl group occurs, giving exclusively the symmetrical 4 : 6-diacetylresorcinol. However, in the isomeric 4-*O*-acetylresacetophenone (VI) the double bonds of the nucleus may be largely stabilised as shown, owing to chelation between the

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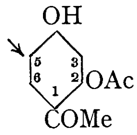
* It is possible that the difference in boiling point between (I) and (II) is more correctly ascribed to molecular architecture rather than to chelation, since the dimethyl ethers of (I) and (II), where chelation is impossible, boil at 187°/15 mm. and 230°/15 mm. respectively. The phenol ethers are, however, sometimes abnormal in their properties; *e.g.*, 3-nitrocatechol is but very weakly associated in dilute benzene solution (*M*, 158·7; theory, 155), whilst its dimethyl ether is very largely associated (*M*, 274·5; theory, 183).

hydroxyl and the nuclear acetyl group, and the *O*-acetyl group should migrate, at least partly, to position 3, giving 2 : 4-diacetylresorcinol (I) (compare migration of acetyl from oxygen to the adjacent *unsaturated* carbon atom in acetoacetic ester, etc.; see Mills and Nixon, *loc. cit.*). This was actually found to be the case,* since migration in (VI) produced by means of aluminium chloride in nitrobenzene gave a 45% yield of mixed diacetylresorcinols (remainder of product was mainly resacetophenone) which consisted of about 58% of 2 : 4-diacetylresorcinol and 42% of 4 : 6-diacetylresorcinol (note that complex formation of the type $>C{=}O{\rightarrow}AlCl_3$ must prevent chelation). This process enables 2 : 4-diacetylresorcinol to be made rapidly and in quantity.† It might be objected that in (V) the acetyl group can migrate to either the para- or the ortho-position, whilst in (VI) it has only the choice of two ortho-positions, and might be expected to migrate almost equally to both. This objection is met by the following experiment. Migration of the *O*-acetyl group in 4-O-*acetyl*-2-O-*methylresacetophenone* (*acetyl*iso*paeanol*) (VII) and methylation of all the resulting phenolic products, gives resacetophenone dimethyl ether and the dimethyl ether of 4 : 6-diacetylresorcinol, but no trace of the easily isolable 2 : 4-*diacetylresorcinol dimethyl ether.* Methylation of the hydroxyl group in (VI) has, therefore, completely prevented the migration of the *O*-acetyl group into position 3. It might be suggested in the latter experiment with (VII) that the further substitution in position 5 is due to the powerful para- and weak ortho-directing influence of the methoxyl as compared with the hydroxyl group in (VI). However, if in (VI) chelation is again prevented by replacing the nuclear acetyl group by the ethyl group, it appears that the *O*-acetyl group migrates quantitatively into position 5 (Rosenmund, Buchwald, and Deligiannis, *loc. cit.*; for constitution of the 6-acetyl-4-ethylresorcinol produced, see Weiss and Kratz, *Monatsh.*, 1929, **51**, 386).



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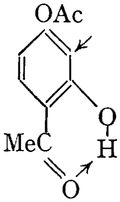

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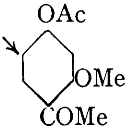
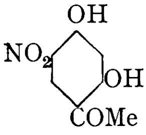


(VII.)



(VIII.)

The reason the double bond is a necessity for chelation is probably to be found in the usual electromeric effect of the two groups concerned. In an *o*-hydroxyacetophenone these effects can set up an electron drift from the singly bound oxygen atom to the doubly bound oxygen atom, provided that the carbon atoms bearing the two groups are doubly bound, and thus bring about the formation of a " neutralised system " (Robinson, *Inst. int. Chim. Solvay, Conseil Chim.*, 1931, **4**, 423) as in (III) and (IV). This drift—to whatever extent it may occur—will make it more easy for the oxygen of the carbonyl group to act as a donor atom, and possibly also more easy for the hydrogen of the hydroxyl group to act as an acceptor, than would otherwise be possible, thus making facile chelation, which in the absence of the double bond would be feeble or impossible.

The remarkably feeble mordant dyeing properties of hydroxy- and polyhydroxy-anthraquinones, where the hydroxyl groups are in the 1, 4, 5, and 8 positions, may be due, if the substances retain a para-quinonoid structure, to the double bonds not being in the correct positions for chelation to occur.

In apparent contradiction to the postulate that chelation between hydroxyl and acetyl is dependent upon the groups being attached to mutually unsaturated carbon atoms, is the fact that the nitration of resacetophenone produces 5-nitroresacetophenone (VIII) and not the isomeric 3-nitro-derivative. Nitration of resacetophenone is, however, preceded by the formation of an addition compound with nitric acid (such addition compounds of nitric

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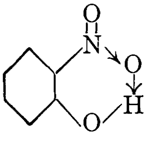
* Rosenmund, Buchwald, and Deligiannis (*loc. cit.*) record the production of 2 : 4-diacetylresorcinol by this reaction, but no experimental details are given.

† A brief account of this work has been given by Professor R. Robinson in the Jubilee Journal of the Society of Dyers and Colourists (1934, p. 76).

acid with ketones have been isolated in a number of cases, *e.g.*, Ph·CO·CH_3,HNO_3; Ph_2CO,HNO_3; $(C_6H_4)_2CO$,HNO_3, etc.; Reddelien, *J. pr. Chem.*, 1915, **91**, 213), and whatever the exact nature of the complex in which the nitric acid is united with the carbonyl group, its formation must prevent chelation between the acetyl and the hydroxyl group, so that the double bonds in the benzene nucleus are not stabilised and nitration will occur in the symmetrical position 5. The position of the nitro-group in nitroresacetophenone (Nencki and Sieber, *J. pr. Chem.*, 1881, **23**, 150) was established by oxidation with hydrogen peroxide in alkaline solution and methylation of the product (compare Baker, *loc. cit.*), 5-nitrohydroxyquinol trimethyl ether being produced, identical with that prepared by the direct nitration of hydroxyquinol trimethyl ether. The nitropaeanol of Adams (*J. Amer. Chem. Soc.*, 1919, **41**, 263) was shown to have a similar orientation, since its methyl ether is identical with the *dimethyl* ether of 5-nitroresacetophenone (*5-nitro-2 : 4-dimethoxyacetophenone*); it is therefore 5-nitro-2-hydroxy-4-methoxyacetophenone.

Chelation in the Nitrophenols.—The *o*-nitrophenols are known to be chelated compounds, but it has not been previously recognised that both oxygen atoms of the nitro-group can act as donors. The donor link must first be produced between the hydrogen of the hydroxyl group and the co-ordinately linked oxygen (since this possesses six free electrons, while the doubly linked oxygen possesses only four) (IX), and this link cannot depend for its formation upon an electromeric transfer from the hydroxyl group, since a co-ordinately linked oxygen atom cannot increase the number of its free electrons in this way. The doubly bound oxygen atom should then be capable of acting as a donor towards a second adjacent hydroxyl group if there is a double bond between the carbon atoms bearing the nitro-group and this hydroxyl group (compare chelation between hydroxyl and acetyl). Thus in 2-nitroresorcinol (X) there is the possibility of a double chelation, and this is fully confirmed by the properties of the compound. It is completely unimolecular in dilute benzene solution at the freezing point (*M*, 151; theory, 155; compare *o*-nitrophenol, which under the same conditions has *M*, 135; theory, 139), very easily volatile in steam and sublimable, soluble in light petroleum, and has a considerably lower boiling point (234°) than resorcinol (281°), and its melting point is lowered only 3·7° under water (compare *o*-, *m*-, and *p*-nitrophenols, whose melting points are lowered by 1°, 54·5°, and 74·4° respectively; Sidgwick, Spurrell, and Davies, *loc. cit.*). The group present in 2-nitroresorcinol always appears to be associated with a bright red colour when, as in this compound itself, the nitro-group is doubly chelated. Both 2-nitroresorcinol and nitrophloroglucinol are red, whilst, though the same group is present in, *e.g.*, styphnic acid (yellow), 2-nitro-4 : 6-diacetylresorcinol (colourless), 2 : 4-dinitroresorcinol (yellow), and trinitrophloroglucinol (yellow), the second chelation of the nitro-group need not be called upon, even if the substances are fully chelated.*



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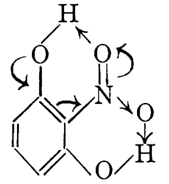

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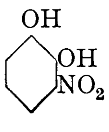

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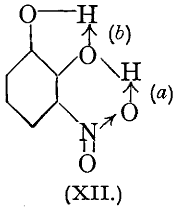

(XII.)

It follows from the double chelation of 2-nitroresorcinol that a nitro-group can chelate with a hydroxyl group when the carbon atoms to which these groups are united are either singly or doubly bound. We have thus a type of chelation essentially different from that between hydroxyl and acetyl, in that the latter depends on the presence of a double bond between the carbon atoms bearing the groups, whilst the former is independent of this. One would, therefore, expect to find no appreciable difference in properties between the isomeric 2 : 4- and 4 : 6-dinitroresorcinols, and actually no such striking differences exist

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* Dischendorfer (*Monatsh.*, 1933, **62**, 263) has prepared a mononitro-4 : 6-dibenzoylresorcinol which he regards as the 5-nitro-derivative, since, unlike 2-nitroresorcinol, it is only weakly yellow. It is clear, however, that this argument is valueless and the compound is without doubt the 2-nitro-derivative.

as are shown by the isomeric diacetylresorcinols. Preliminary examination has shown that both compounds are but rather weakly chelated.

3-Nitrocatechol (XI) affords another interesting case of chelation. It is an orange-yellow substance with a powerful nitrophenolic odour, very readily volatile in steam, readily soluble in light petroleum, and is only slightly associated in benzene (see footnote, p. 1685). It has a lower boiling point (231°) than catechol (245°), and is obviously more fully chelated than this compound, which shows a considerably greater association in benzene (Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 860, 1316). The low boiling point is remarkable when it is recalled that the introduction of the nitro-group into the ortho-position of phenol raises the boiling point from 182° to 215°, notwithstanding the powerful chelation of *o*-nitrophenol. 3-Nitrocatechol is, therefore, best represented by (XII), in which the donor link (*a*) helps the formation of the donor link (*b*) between the two hydroxyl groups, these groups being consequently more chelated than in catechol. The same effect seems to occur also in 2 : 3-dihydroxybenzaldehyde (Pauly and Lockemann, *Ber.*, 1910, **43**, 1813; Pauly, Schübel, and Lockemann, *Annalen*, 1911, **383**, 312), whose boiling point is 10° lower than that of catechol (introduction of the aldehyde group into the ortho-position of phenol raises the boiling point by 15°).

Disubstitution in the Resorcinol Nucleus.

Disubstitution in the resorcinol nucleus may lead either to 2 : 4- or to 4 : 6-disubstituted resorcinols. Both types of substitution are quite distinct; only in one case (diacetylresorcinols; already discussed) have both isomerides been isolated from the same reaction. Moreover, in all cases the 4-monosubstituted resorcinol is first produced, followed by the introduction of the second group into position 2 or 6. Very few instances of direct substitution in position 2 in resorcinol itself are recorded, and in all cases a very much greater quantity of the 4-substituted resorcinol is simultaneously produced (see coupling of diazonium salts with resorcinol, Wallach and Fischer, *Ber.*, 1882, **15**, 2817; Will and Puckall, *Ber.*, 1887, **20**, 1121, 1145; Bechold, *Ber.*, 1889, **22**, 2377; formation of 2 : 6-dihydroxybenzoic acid, Senhöfer and Brunner, *Wien Akad. Wiss.*, 1879, **80**, 504; Brunner, *Annalen*, 1906, **351**, 313; formation of 2-nitroresorcinol, Weselsky and Benedikt, *Monatsh.*, 1880, **1**, 894 : see also Chapman and Stephen, J., 1925, **127**, 885; Dischendorfer, *loc. cit.*). Among already disubstituted resorcinols, a unique position is occupied by 4 : 5-dimethoxyresorcinol, which reacts only in position 2 (Baker, Nodzu, and Robinson, J., 1929, 76; Baker and Robinson, *ibid.*, p. 153), this curious result being undoubtedly associated with the extremely powerful para-directing influence of the veratrole group.

The following table gives those (unmixed) disubstitution products which can be obtained either by direct introduction of groups into resorcinol, or by migration from the oxygen atoms, the relevant references in each case being appended.

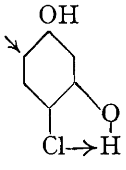
Disubstituted Resorcinols.

Positions 2 : 4- :	—	—	—	—	—	—	NO[7]	CHO[8]	$CO{\cdot}CH_3$[9]	$CO{\cdot}R$[11]	$N{:}NAr$[13]
Positions 4 : 6- :	Cl[1]	Br[2]	I[3]	SO_3H[4]	CO_2H[5]	$CH_2{\cdot}CH{:}CH_2$[6]	—	—	$CO{\cdot}CH_3$[10]	$CO{\cdot}R$[12]	$N{:}NAr$[14]

[1] Mettler, *Ber.*, 1912, **45**, 802; Weiss and Kratz, *Monatsh.*, 1929, **51**, 386. [2] Zehenter, *Monatsh.*, 1887, **8**, 296. [3] Nicolet and Sampey, *J. Amer. Chem. Soc.*, 1927, **49**, 1796; definite proof of this orientation is lacking. [4] Kaufmann and de Pay, *Ber.*, 1904, **37**, 725. [5] Späth, Klager, and Schlösser, *Ber.*, 1931, **64**, 2206. [6] Hurd, Greengard, and Pilgrim, *J. Amer. Chem. Soc.*, 1930, **52**, 1700; definite proof of this orientation is lacking. [7] von Kostanecki, *Ber.*, 1887, **20**, 3133; Orndorff and Nichols, *J. Amer. Chem. Soc.*, 1923, **45**, 1536. [8] Baker, Kirby, and Montgomery, J., 1932, 2876. [9] By rearrangement of 4-*O*-acetylresacetophenone and of resorcinol diacetate, accompanied by the 4 : 6-isomeride; this paper; Rosenmund, Buchwald, and Deligiannis, *loc. cit.* [10] By migration of resorcinol diacetate or of 2-*O*-acetylresacetophenone; for references see Baker, *loc. cit.*; also as under [9]. [11] Rosenmund, Buchwald, and Deligiannis, *loc. cit.* [12] Wittig and Richter, *Ber.*, 1926, **59**, 116; Klarmann, *J. Amer. Chem. Soc.*, 1926, **48**, 2358. [13] Coupling in very weakly alkaline, neutral, or acid solution; Liebermann and von Kostanecki, *Ber.*, 1884, **17**, 880; von Kostanecki, *Ber.*, 1887, **20**, 3137; Orndorff and Ray, *Amer. Chem. J.*, 1910, **44**, 1. [14] In solutions of caustic alkalis; von Kostanecki, *Ber.*, 1888, **21**, 3117; Orndorff and Ray, *loc. cit.*

The position taken up by the second entering atom or group depends primarily on the nature of the first substituent in position 4, and, in the absence of disturbing factors, the second substituent enters position 6 to give the symmetrical 4 : 6-disubstituted resorcinol, and the extremely rare substitution of resorcinol in position 2 does not occur. A brief account of these substitutions may now be given.

Dihalogenoresorcinols.—The intermediate 4-halogenoresorcinols (as XIII) are feebly chelated (Sidgwick, J., 1920, **117**, 389; Sidgwick and Turner, J., 1922, **121**, 2256; Sidgwick and Callow, *loc. cit.*), but such chelation cannot depend upon an electromeric transfer (thus stabilising the double bonds as in the case of hydroxyl and acetyl), since a halogen atom cannot increase the number of its free electrons in this way (compare the co-ordinately linked oxygen of the nitro-group). The second halogen atom will therefore enter the normal position 6.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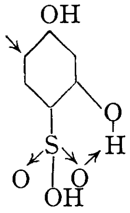
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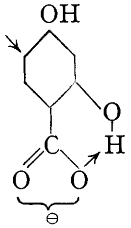
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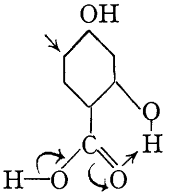
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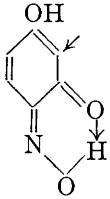
Resorcinoldisulphonic Acid.—Resorcinol-4-sulphonic acid (XIV), even if chelated, must substitute in position 6, since, as in the case of the halogens, chelation cannot require the fixation of the double bonds of the nucleus.

Resorcinoldicarboxylic Acid.—Two carboxyl groups may be introduced into resorcinol by heating with aqueous sodium bicarbonate under pressure, or by similar methods. The intermediate resorcinol-4-carboxylic acid (β-resorcylic acid) will be present in its ionised form (XV), which may or may not be chelated. In either case the double bonds in the nucleus are left free to move (compare the first chelation of the nitro-group, and the chelation of the halogen compounds) and the second carboxyl group will enter position 6. Even in its non-ionised form (XVI), whether chelated or not, β-resorcylic acid must substitute in position 6; the chelation between the carbonyl group and the adjacent phenolic hydroxyl group will be made possible as the result of electromeric change within the carboxyl group as indicated, and the electromeric drift from the phenolic oxygen (with consequent fixing of the double bonds) will not be called upon. Thus, in no circumstances will chelation between a carboxyl (or carboxylic ester) and a hydroxyl group require the presence of a double bond in the nucleus. This view harmonises with the facts that β-resorcylic acid is chlorinated, brominated, and nitrated in position 6.

Diallylresorcinol.—This compound is prepared by intramolecular rearrangement from resorcinol diallyl ether. The intermediate 4-allylresorcinol monoallyl ether, whether the 2- or the 4-*O*-ether, contains no features which would cause substitution to occur in position 2. It may, therefore, be prophesied with confidence that diallylresorcinol is the 4 : 6-derivative.

Dinitrosoresorcinol.—The dinitrosation of resorcinol is effected in weakly acid solution, and the intermediate 4-nitrosoresorcinol (Barberio, *Gazzetta*, 1907, **37**, 577) is produced in the free condition. It is not known whether this intermediate nitrosoresorcinol is to be regarded as such or as a quinonemonoxime, but the *o*-nitrosophenols are chelated (2 : 4-dinitrosoresorcinol is volatile in steam and a mordant dye) and whether 4-nitrosoresorcinol is chelated as a quinonemonoxime (XVII) or a nitrosophenol (XVIII) (these are electromerides and therefore identical) the double bonds of the benzene nucleus are fixed, and nuclear activation by the hydroxyl group in position 1 can take place in position 2 but not in position 6 [unless in (XVIII) the activation, in a very unlikely manner, is transmitted right round the nucleus]. Further nitrosation will occur, therefore, in position 2, with production of 2 : 4-dinitrosoresorcinol. The *p*-quinonemonoxime structure of 4-nitrosoresorcinol corresponding to (XVII) would also lead to further substitution in position 2, in this case the activating group being the hydroxyl in position 3.



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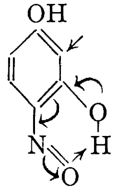

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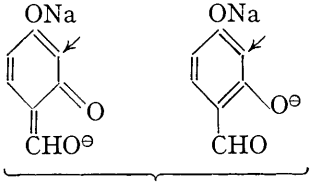

(*a*) (*b*)

(XIX.)

Resorcinol-2 : 4-*dialdehyde.*—This is prepared by the Tiemann–Reimer reaction and isolated in very poor yield by steam distillation from the complex reaction product. By analogy with 2 : 4- and 4 : 6-diacetylresorcinols, only the former of which is appreciably volatile in steam, resorcinol-4 : 6-dialdehyde should be but very slightly volatile, and if produced during the reaction, would not be isolated in quantity. The 2 : 4-dialdehyde is, however, isolated in a state of purity, and it is therefore probable that the 4 : 6-dialdehyde is produced, if at all, only in minute trace. The resorcinol-2 : 4-dialdehyde is doubtless produced in the following manner. The intermediate resorcinol-4-aldehyde in strongly alkaline solution is probably the half-ionised disodium salt, best represented as an equilibrium between the tautomeric electromerides (XIX), the form (*a*) being derived from the ortho-quinonoid keto-oxymethylene form (such compounds are powerful acids, *e.g.*, oxymethyleneacetoacetic ester; it is possible that certain *o*-hydroxy-aldehydes may exist in the keto-oxymethylene form even in the free state, *e.g.*, *m*-xylorcylaldehyde, Robertson and Robinson, J., 1927, 2197). The structure is exactly analogous to that of the ionised carboxyl group, except that in this case the group is extended by the addition of C:C. Forms (*a*) and (*b*) represent the two possible extremes; any departure from (*b*) must cause the fixation of the double bonds as indicated and lead to substitution in position 2. The para-quinonoid structure corresponding to (XIX) can also be reactive only in position 2 [compare the para-quinonoid structure corresponding to (XVII) already mentioned].

Diacylresorcinols.—The diacetylresorcinols have already been considered, and may be taken as typical of this group of compounds, the arguments being unaffected if the rearrangement is inter- rather than intra-molecular. The recent preparation of 2 : 4-diacetylresorcinol by direct rearrangement of resorcinol diacetate in presence of aluminium chloride below 130° (Rosenmund, Buchwald, and Deligiannis, *loc. cit.*) probably proceeds *via* 2- and 4-*O*-acetylresacetophenones, the former being converted into 4 : 6-diacetylresorcinol, and the latter undergoing the previously discussed rearrangement with production of 2 : 4-diacetylresorcinol.

Bisazoresorcinols.—Except in strongly alkaline solution, coupling occurs in positions 2 and 4. Under these conditions the intermediate 4-azo-derivative probably largely exists in the *o*- or *p*-quinonehydrazone form (compare 4-nitrosoresorcinol); in either case further substitution must occur in position 2, which is activated by the free hydroxyl group. In strongly alkaline solution, however, the compound will exist as the half-ionised disodium salt of the true azo-compound (note that simple azo-compounds such as *o*-hydroxyazobenzene as distinct from, *e.g.*, azo-β-naphthol are easily soluble in alkaline solutions) which, independently of the position of the negative charge, will undergo further substitution in the symmetrical position 6. These explanations are not regarded as final, since cases are known where the position taken up by an entering arylazo-group depends upon the nature of the diazonium ion.

EXPERIMENTAL.

2 : 4-*Diacetylresorcinol* (I).—When 4-*O*-acetylresacetophenone (100 g., crystallised from methyl alcohol; Baker, J., 1933, 1385), lump aluminium chloride (100 g.), and nitrobenzene (200 c.c.) were warmed to 70° with gentle agitation, a fairly vigorous reaction set in and the temperature rose to about 115°. After the product had cooled to 70°, it was heated with water (500 c.c.) and concentrated hydrochloric acid (250 c.c.) on the steam-bath till the aluminium

chloride complex had decomposed. The nitrobenzene layer was run off, the residual liquid extracted with a little carbon tetrachloride, the nitrobenzene and the extract united and shaken with concentrated hydrochloric acid (100 c.c.), then with a little water, and the phenolic products extracted by shaking twice with 10% sodium hydroxide solution (400 c.c. and 100 c.c.). The alkaline liquids were shaken with a little ether, acidified with hydrochloric acid, and cooled to 0°, and the solid product was collected after a few hours, crushed under methyl alcohol (100 c.c.), washed with methyl alcohol (50 c.c.), dried at a moderate temperature (yield, 50 g. of a very pale brown, crystalline product), and briskly extracted (Soxhlet) with light petroleum (400 c.c.; b. p. 60—80°) for 1 hour. Crystalline 2 : 4-diacetylresorcinol (26·3 g., m. p. 85—87°) separated in the flask. The residue in the thimble (about 19 g.) was a mixture of 4 : 6- and 2 : 4-diacetylresorcinol which could not be efficiently separated.

2 : 4-*Diacetylresorcinol Dimethyl Ether.*—To 2 : 4-diacetylresorcinol, covered with acetone, methyl sulphate (very large excess) and 30% potassium hydroxide solution were alternately added, the mixture being allowed to boil. Extraction of the alkaline liquid with ether yielded an oil, which solidified and then separated from light petroleum (b. p. 40—60°) in prismatic needles, m. p. 65°, b. p. 187°/15 mm. (Found : C, 64·8; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%).

Resacetophenone 2-O-*Methyl Ether* (iso*Paeanol*).—(A) Resorcinol monomethyl ether was shaken in sodium hydroxide solution with acetic anhydride at 0°, and the product distilled in a vacuum. The acetyl derivative (37 g.) in nitrobenzene (50 c.c.), and aluminium chloride (37 g.) were heated to 50°; a fairly vigorous reaction then set in and the temperature was kept at about 90°. After ½ hour, the product was decomposed by dilute hydrochloric acid and steam-distilled for 5 hours. The distillate yielded paeanol (21·6 g.); the remaining liquor was extracted with warm benzene and yielded, after crystallisation from water (charcoal), *iso*paeanol, m. p. 138° (1·6 g.). (B) A mixture of resorcinol monomethyl ether (100 g.), acetonitrile (60 g.), zinc chloride (40 g.), and ether (400 c.c.) was saturated with hydrogen chloride (Hoesch, *Ber.*, 1915, **48**, 1122). After 2 days the ketimine was completely precipitated by the addition of fresh ether, and was hydrolysed by heating for 4 hours with dilute hydrochloric acid under benzene. The benzene layer yielded a pasty mixture of paeanol and *iso*paeanol, which, after crystallisation from the minimum quantity of a 50% mixture of chloroform and carbon tetrachloride, yielded *iso*paeanol (9·2 g.). The non-crystalline product was distilled in steam, the distillate yielding paeanol (15 g.) and the residue a further quantity of *iso*paeanol (4 g.).

iso*Paeanol Acetate.*—*iso*Paeanol, acetic anhydride, and sodium acetate were boiled for 2 hours, the product shaken with water and extracted with ether, and the extracts shaken with sodium carbonate solution, dried, and distilled under diminished pressure. The distillate solidified on cooling, and, after washing with ligroin, had m. p. 34° (Found : C, 63·8; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

Migration of iso*Paeanol Acetate.*—*iso*Paeanol acetate (10 g.), nitrobenzene (20 c.c.), and aluminium chloride (10 g.) were warmed to 70°; a gentle reaction then set in, the temperature rising to 90°. The product was decomposed by heating with water (50 c.c.) and concentrated hydrochloric acid (25 c.c.) and extracted with chloroform, and the mixture of phenolic products separated from the chloroform by shaking with 10% sodium hydroxide solution. This was then methylated with a very large excess of methyl sulphate and alkali under acetone, and yielded an oil which was steam-distilled for several hours. From the distillate, ether extracted resacetophenone dimethyl ether, m. p. 37° (the pure substance has m. p. 40°); the product could therefore contain at most only a minute trace of 2 : 4-diacetylresorcinol dimethyl ether, which is easily volatile in steam. The residue from the steam distillation consisted of 4 : 6-diacetylresorcinol dimethyl ether, m. p. 171°, and a further quantity of resacetophenone dimethyl ether.

5-*Nitroresacetophenone.*—Resacetophenone (20 g.) was shaken with nitric acid (100 c.c.; *d* 1·42) at 30—40°. After 10 minutes, water was added and the solid was collected, washed, and crystallised from methyl alcohol (charcoal), forming amber-coloured prisms (9 g.), m. p. 142° (compare Nencki and Sieber, *loc. cit.*).

5-*Nitrohydroxyquinol Trimethyl Ether.*—5-Nitroresacetophenone (8 g.) in *N*-sodium hydroxide (160 c.c.) was treated with 3% hydrogen peroxide (100 c.c.) in an atmosphere of coal gas. The temperature rose from 18° to 42° and after an hour the liquid was acidified, cooled to 0°, filtered from unchanged resacetophenone (0·3 g.), and extracted six times with ether. The extracts yielded a brownish-orange crystalline residue (3·5 g.) of 5-nitrohydroxyquinol, which was directly methylated with methyl sulphate and potassium carbonate in acetone for 10 minutes. After heating with water, and addition of dilute sodium hydroxide solution, ether extracted 5-nitrohydroxyquinol trimethyl ether, which separated from alcohol in thin yellow needles, m. p. 131°

(alone or mixed with a specimen prepared by the direct nitration of hydroxyquinol trimethyl ether).

5-*Nitroresacetophenone Dimethyl Ether*.—(a) 5-Nitroresacetophenone was methylated in alcohol by vigorous treatment with a large excess of methyl sulphate and aqueous potassium hydroxide. The solid crystallised from alcohol, in which it was sparingly soluble, in small prismatic needles, m. p. 180° (Found : C, 53·5; H, 5·1; N, 6·3. $C_{10}H_{11}O_5N$ requires C, 53·3; H, 4·9; N, 6·2%). The same compound (mixed m. p.) was also produced by the methylation of nitropaeanol (Adams, *loc. cit.*). A compound, m. p. 131°, supposed to be nitropaeanol methyl ether (Found : N, 6·2%), is described by Adams, but it is clear that the compound must possess some other constitution. The substance turned yellow-red on exposure to light, and with phenylhydrazine in alcohol gave at once nitropaeanol phenylhydrazone, so that methylation could not have occurred under the mild conditions employed.

2-*Nitro*-4 : 6-*diacetylresorcinol*.—4 : 6-Diacetylresorcinol (4 g.) and nitric acid (40 c.c.; *d* 1·42) were warmed to 80°; a gentle reaction then set in, and the temperature was kept just below 80°. After 2 hours at room temperature, the liquid was diluted, and the solid recrystallised from alcohol, in which it was very sparingly soluble, forming thick hexagonal plates, m. p. 235° (decomp.) (Found : C, 50·4; H, 3·7; N, 5·6. Calc. for $C_{10}H_9O_6N$: C, 50·2; H, 3·8; N, 5·8%). Its alcoholic solution gives a bright orange-red colour with ferric chloride. With aqueous sodium hydroxide the crystals are coloured orange, and dissolve to give a yellow solution. Adams (*loc. cit.*) describes the substance as white needles, m. p. 231°.

3-*Nitrocatechol*.—3-Nitroveratrole (10 g.; Baker and Smith, J., 1931, 2548) was refluxed for 12 hours with acetic acid (50 c.c.) and hydrobromic acid (50 c.c.; *d* 1·5). The product was poured into water (300 c.c.), extracted with ether, dried, and distilled under diminished pressure, and the solid 3-nitrocatechol was recrystallised from light petroleum (b. p. 60—80°) and obtained as quinone-coloured prismatic needles (7 g.), m. p. 86°.

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