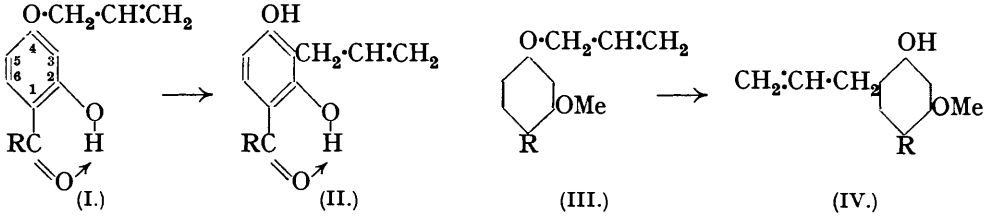
60. *Studies in Chelation. Part III. The Stabilisation of Kekulé Forms in* o-*Hydroxy-carbonyl Compounds.*

By Wilson Baker and (Miss) O. M. Lothian.

It was shown in Part II (Baker and Lothian, J., 1935, 628) that the thermal rearrangement of 4-*O*-allylresacetophenone gave 3-allylresacetophenone, and that the rearrangement of 2-*O*-methyl-4-*O*-allylresacetophenone gave the differently oriented 2-*O*-methyl-5-allylres-

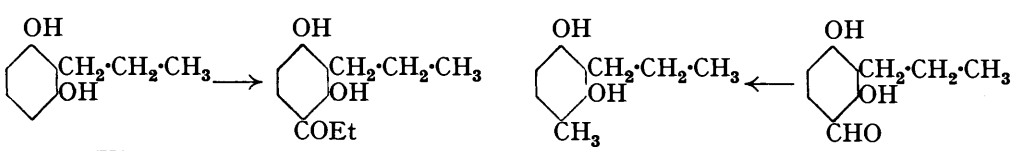
acetophenone. This behaviour was anticipated on the view that chelation between the hydroxyl and the acetyl group in *o*-hydroxyacetophenones depends upon the mutual unsaturation of the carbon atoms bearing these groups (see Part I; Baker, J., 1934, 1684) and therefore leads to stabilisation of one of the Kekulé forms, and in the rearrangement of 4-*O*-allylresacetophenone to the exclusive formation of 3-allylresacetophenone. In 2-*O*-methyl-4-*O*-allylresacetophenone, chelation is prevented by methylation, no stabilisation of Kekulé forms occurs, and migration of the allyl group leads to the symmetrical type of product usually given by resorcinol derivatives.

The same effect has now been found to occur in *o*-hydroxy-propiophenones and in *o*-hydroxy-aldehydes. 4-O-*Allylrespropiophenone* (I; R = Et) underwent molecular rearrangement on heating to give an 85% yield of 3-*allylrespropiophenone* (II; R = Et) as the only isolable compound. 2-O-*Methyl*-4-O-*allylrespropiophenone* (III; R = COEt) similarly gave an 80% yield of 2-O-*methyl*-5-*allylrespropiophenone* (IV; R = COEt), and in this case also no other product could be isolated.



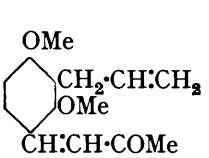
Of β-resorcylaldehyde derivatives, 4-O-*allyl*-β-*resorcylaldehyde* (I; R = H) underwent thermal rearrangement to give a 50% yield of 3-*allyl*-β-*resorcylaldehyde* (II; R = H) as the only isolable compound, and 2-O-*methyl*-4-O-*allyl*-β-*resorcylaldehyde* (III; R = CHO) gave a 59% yield of 2-O-*methyl*-5-*allyl*-β-*resorcylaldehyde* (IV; R = CHO). The poorer yields of the aldehyde derivatives are due to the reactive nature of the aldehyde group.

The derivatives of respropiophenone were prepared and oriented in the following manner. Allylation of respropiophenone in acetone solution with allyl bromide and potassium carbonate gave the 4-*O*-allyl ether (I; R = Et), the position of the allyl group being proved by the formation of a chelate *copper* derivative soluble in chloroform. The position of the allyl group in 3-allylrespropiophenone was proved by catalytic reduction to 3-n-*propylrespropiophenone* (VI), a compound which was independently synthesised from 2-*n*-propylresorcinol (V) (Part II, *loc. cit.*) and propionitrile under the conditions of the Hoesch synthesis. Methylation of (I; R = Et) in acetone solution with methyl sulphate gave the methyl ether (III; R = COEt). The position of the allyl group in (IV; R = COEt) was established by conversion into the methyl ether, *5-allylrespropiophenone dimethyl ether*, m. p. 67°, which was not identical with the dimethyl ether of (II; R = Et), *3-allylrespropiophenone dimethyl ether*, b. p. 180°/18 mm.

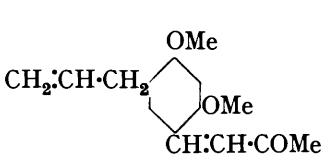


β-Resorcylaldehyde was converted by allylation into the 4-*O*-allyl ether (I; R = H), and thence by methylation into (III; R = CHO). The last compound was also produced by allylation of the known 2-*O*-methyl ether of β-resorcylaldehyde, a fact which proves the position of the allyl group in (I; R = H). The orientation of (II; R = H) was established by catalytic reduction in presence of palladium chloride, both the allyl group and the aldehyde group being completely reduced with formation of 4-*methyl*-2-n-*propylresorcinol* (VII), a compound which was independently synthesised from 2-*n*-propylresorcinol by conversion into 3-n-*propyl*-β-*resorcylaldehyde* (VIII), and subsequent catalytic reduction.

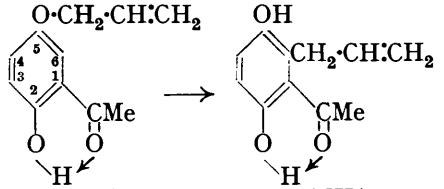
Methylation of (II; R = H) and (IV; R = CHO) with methyl sulphate and alkali in acetone solution led to the two isomeric compounds 2 : 4-*dimethoxy*-3-*allylstyryl methyl ketone* (IX), m. p. 45°, and 2 : 4-*dimethoxy*-5-*allylstyryl methyl ketone* (X), m. p. 76°, the non-identity of which proves the position of the allyl group in (IV; R = CHO). The complete methylation of (II; R = H) in the absence of acetone presented difficulties, and in presence of acetone the methylated styryl methyl ketone was obtained, the same condensation taking place in the case of (IV; R = CHO); solid isomeric products were thus obtained for direct comparison.



(IX.)

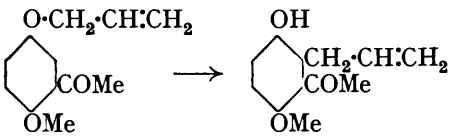


(X.)

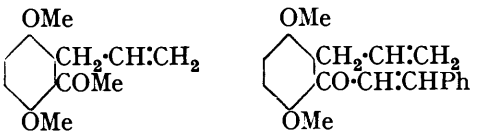


(XI.) (XII.)

An attempt was made to detect the possible fixation of a Kekulé form in 2 : 5-dihydroxyacetophenone (quinacetophenone) in a similar manner. Molecular rearrangement of 2-*hydroxy*-5-*allyloxyacetophenone* (XI) yielded 2 : 5-*dihydroxy*-6-*allylacetophenone* (XII) in 74% yield in accordance with expectations. From 2-*methoxy*-5-*allyloxyacetophenone* (XIII), the methyl ether of (XI) in which chelation is impossible, was, however, obtained in 94% yield the methyl ether of (XII), namely, 5-*hydroxy*-2-*methoxy*-6-*allylacetophenone* (XIV). The "natural" position of substitution in non-chelate derivatives of 2 : 5-dihydroxyacetophenone is hence identical with the position of substitution to be expected on the grounds of a fixed Kekulé structure as in (XI), unlike the case of the resorcinol derivatives previously studied. These experiments, therefore, do not afford evidence of a stable Kekulé form in 2 : 5-dihydroxyacetophenone, but are entirely in harmony with the view that such a stable form exists.



(XIII.) (XIV.)



(XV.) (XVI.)

Allylation of quinacetophenone gave the 5-*O*-allyl ether (XI), the compound being shown to be an *o*-hydroxyacetophenone by the formation of a chelate copper derivative. Methylation of (XI) yielded (XIII). The similar orientation of (XII) and (XIV) was shown by the fact that on methylation they both gave 2 : 5-*dimethoxy*-6-*allylacetophenone* (XV) (liquid), characterised in each case by the formation of the benzylidene derivative, 2 : 5-*dimethoxy*-6-*allylphenyl styryl ketone* (XVI). The position occupied by the nuclear allyl group in these compounds followed from the fact that under no conditions could 2 : 5-dimethoxy-6-allylacetophenone (XV) be converted into a semicarbazone, the suppression of carbonyl reactivity being obviously due to steric influences. Such influences could be operative only if the allyl group occupied position 6. The correctness of this view was established by the fact that the isomeric 2 : 4-dimethoxy-3-allylacetophenone yielded a *semicarbazone* with extreme ease, as do all the known dimethoxyacetophenones.

In attempts to apply the present methods to derivatives of 4-ethylresorcinol, β-resorcylic acid, 4-nitroresorcinol, and nitroquinol, the following compounds were prepared: 4-*ethylresorcinol diacetate*; 4-*ethylresorcinol diallyl ether*; 4-O-*allyl*-β-*resorcylic acid*; *ethyl* 4-O-*allyl*-β-*resorcylate*; 4-*nitroresorcinol* 1-O-*allyl ether*; 4-*nitro*-6 (or 2)-*allylresorcinol*; *nitroquinol diallyl ether*; 2-*nitroquinol* 4-O-*allyl ether*. In these cases the rearrangement of the allyl ethers did not take place sufficiently smoothly to warrant a continuation of the experiments.

Experimental.

4-O-*Allylrespropiophenone* (I; R = Et).—A mixture of respropiophenone (73 g.; 1 mol.; dried in a vacuum over sulphuric acid), anhydrous potassium carbonate (80 g.), and allyl bromide (54 g.; 1 mol.) in acetone (160 c.c.) was refluxed and stirred on the water-bath for 7 hours. After acidification the product was extracted with ether, and precipitated therefrom as the very sparingly soluble sodium salt by shaking with 10% aqueous sodium hydroxide (700 c.c.). The salt was collected on a sintered glass funnel, washed with ether, and decomposed by the addition of hydrochloric acid. The liberated 4-O-*allylrespropiophenone* was taken up in ether and isolated as a colourless oil, b. p. 174°/14 mm. (Found: C, 69·6; H, 6·7. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·9%). It gave an intense reddish-brown coloration with alcoholic ferric chloride.

The *copper* derivative was prepared by shaking a solution of the compound (2 g.) in alcohol (20 c.c.) with saturated aqueous copper acetate (40 c.c.) containing 2 drops of dilute aqueous ammonia. The green product, which solidified completely on rubbing, was collected, washed with water and then alcohol, and to the filtered solution in warm chloroform (10 c.c.) was added alcohol (10 c.c.). The copper derivative separated in blue-green prismatic needles, m. p. 158° (darkening and partial decomposition) (Found: C, 59·9; H, 5·8; Cu, 12·2. $C_{24}H_{26}O_6Cu$,EtOH requires C, 60·0; H, 6·2; Cu, 12·2%. The presence of alcohol was proved qualitatively by heating).

3-*Allylrespropiophenone* (II; R = Et).—4-*O*-Allylrespropiophenone (3·6 g.) was heated in an oil-bath at 205° for 2 hours. The product crystallised completely on cooling to an almost white mass, m. p. 114—118°. A quantity (3·4 g.) of this crude product, crystallised from benzene–light petroleum (b. p. 40—60°) (40 c.c. of each), yielded colourless material (2·4 g.), m. p. 123—124°. By working up the mother-liquor, a further quantity (0·6 g.) of slightly crude product, m. p. 118—120°, was obtained. The results show that the total yield is not less than 85%. Pure 3-*allylrespropiophenone* separated from benzene–ligroin in small plates, m. p. 124° (Found: C, 69·7; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·9%). Its alcoholic or dilute alcoholic solution gave an intense purplish-brown colour with ferric chloride.

3-n-*Propylrespropiophenone* (VI).—(A) A mixture of 2-*n*-propylresorcinol (1 g.) (Baker and Lothian, *loc. cit.*), propionitrile (2 c.c.), dry ether (20 c.c.), and anhydrous zinc chloride (1 g.) was saturated with hydrogen chloride at 0°. After 24 hours, addition of water threw down a very sparingly soluble zinc-containing derivative of the ketimine, which was not hydrolysed by heating with dilute hydrochloric acid containing zinc chloride. After separation from the acid solution it was, however, rapidly hydrolysed by heating with water, and the *ketone* separated as an oil which became solid on cooling (1·1 g.). It separated from very dilute alcohol in colourless nacreous plates, m. p. 109—110° (Found: C, 68·9; H, 8·0. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). (B) 3-Allylrespropiophenone (1 g.) was reduced in alcohol (15 c.c.) with hydrogen in presence of palladium chloride (0·15 g.). Absorption of hydrogen was complete in 1 hour, and evaporation of the filtered solution left a solid, which was crystallised first from light petroleum (b. p. 60—80°) and then from dilute alcohol and obtained in nacreous plates, m. p. 109—110° either alone or when mixed with that prepared by method (A).

3-*Allylrespropiophenone Dimethyl Ether*.—3-Allylrespropiophenone (2·5 g.) in acetone (50 c.c.) was shaken with the alternate addition of methyl sulphate (25 c.c.) and excess of 20% potassium hydroxide solution, the mixture being finally heated on the water-bath for ½ hour. An ethereal extract of the product was washed with 20% potassium hydroxide solution, then with water, dried, and distilled, leaving an oil, b. p. 180°/18 mm., $n_D^{15°}$ 1·540 (Found: C, 71·8; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

2-O-*Methyl*-4-O-*allylrespropiophenone* (III; R = COEt).—4-*O*-Allylrespropiophenone (36 g.) was treated in acetone (200 c.c.) with methyl sulphate (100 c.c.) and 20% aqueous potassium hydroxide in the usual manner, the mixture being allowed to boil. After heating on the steam-bath for ½ hour with excess of alkali, the product was diluted, and extracted with ether, and the extracts were shaken with dilute sodium hydroxide solution, dried, and distilled, leaving an oil (38 g.) which solidified on cooling. Its solution in light petroleum (b. p. 40—60°), when cooled to 0°, deposited fibrous needles, m. p. 31° (Found: C, 70·9; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

2-O-*Methyl*-5-*allylrespropiophenone* (IV; R = COEt).—2-*O*-Methyl-4-*O*-allylrespropiophenone was heated for 2 hours at 200°. The pasty product (1·65 g.) was shaken with dilute sodium hydroxide solution and ether; the ethereal layer yielded unchanged material (0·70 g.), m. p. 30—31°; the alkaline layer was acidified, and the crystalline 2-O-*methyl*-5-*allylrespropio-*

phenone collected and dried (yield, 0·95 g.; m. p. about 115°). After crystallisation from a little benzene and then from dilute alcohol (charcoal) it was obtained as fine prismatic needles, m. p. 132—133° (Found: C, 70·9; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The yield of pure product (0·77 g.) was 80% of the theoretical, calculated on the weight of (III; R = COEt) which had undergone rearrangement.

5-*Allylrespropiophenone Dimethyl Ether*.—2-*O*-Methyl-5-allylrespropiophenone in 10% sodium hydroxide solution was shaken with excess of methyl sulphate at about 60°. The alkali-insoluble product solidified on cooling, and was collected, washed, and dried; it crystallised from light petroleum (b. p. 40—60°) in curved prismatic needles, m. p. 67° (Found: C, 71·8; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

4-O-*Allyl*-β-*resorcylaldehyde* (I; R = H).—A mixture of β-resorcylaldehyde (22 g.; 1 mol.), anhydrous potassium carbonate (40 g.), and allyl bromide (19·2 g.; 1 mol.) was refluxed and stirred on the water-bath for 7 hours. After removal of most of the acetone by distillation the residue was acidified with dilute hydrochloric acid and extracted with ether. The ethereal layer was now shaken with 8% sodium hydroxide solution, and β-resorcylaldehyde and its monoallyl ether liberated from the alkaline solution by addition of acid and separated by distillation in steam, in which only the latter was volatile. The steam-distillate yielded 4-O-*allyl*-β-*resorcylaldehyde* (9 g.) as a colourless oil, b. p. 149—150°/13 mm. (Found: C, 67·1; H, 5·4. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). Its alcoholic solution gave an intense reddish-brown coloration with ferric chloride.

3-*Allyl*-β-*resorcylaldehyde* (II; R = H).—4-*O*-Allyl-β-resorcylaldehyde (5 g.) was heated in an oil-bath at 190—200° for 1 hour, the maximum temperature of the melt reaching 202°. The resulting dark red, sticky solid was decolourised by boiling with charcoal in alcoholic solution for 3 hours, and the recovered product recrystallised from carbon tetrachloride (yield, 2·5 g.). It separated in lustrous needles, m. p. 129—130° (Found: C, 67·3; H, 5·7. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%).

2-O-*Methyl*-4-O-*allyl*-β-*resorcylaldehyde* (III; R = CHO).—(A) 4-*O*-Allyl-β-resorcylaldehyde (6 g.) in acetone (150 c.c.) was methylated by the alternate addition of methyl sulphate (55 c.c.) and an excess of 20% aqueous potassium hydroxide in small quantities, the mixture being allowed to boil. After ½ hour the solution was extracted with ether, the extract shaken with 20% potassium hydroxide solution, and distilled, leaving an oil which slowly solidified. The product separated from light petroleum (b. p. 40—60°) in colourless rhombic prisms, m. p. 45° (Found: C, 68·8; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

(B) A mixture of 2-*O*-methyl-β-resorcylaldehyde (2·5 g.) (Gattermann and Berckelmann, *Ber.*, 1898, **31**, 1767), acetone (150 c.c.), potassium carbonate (15 g.), and allyl bromide (5 g.) was stirred under reflux on the water-bath for 6 hours. After removal of the acetone by distillation and addition of dilute aqueous sodium hydroxide, the solution yielded to ether a solid (3·1 g.), which, after crystallisation as before, formed prisms, m. p. 44—45°, not depressed by the specimen prepared by method (A).

2-*Methoxy*-4-*allyloxystyryl methyl ketone* was produced on one occasion in place of compound (III; R = CHO) in experiment (A) (above). It formed pale yellow crystals, m. p. 39—40°, from light petroleum (Found: C, 72·4; H, 7·0. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·8%). When mixed with (III; R = CHO), it melted at 25—30°.

2-O-*Methyl*-5-*allyl*-β-*resorcylaldehyde* (IV; R = CHO).—2-*O*-Methyl-4-*O*-allyl-β-resorcylaldehyde (1·83 g.) was heated at 220° for 1 hour, the maximum temperature reached by the melt being 203°. The dark semi-solid product was dissolved in ether, and the solution shaken with aqueous sodium hydroxide. The ether yielded unchanged initial material (0·67 g.), and the alkaline solution after acidification yielded to ether a rather dark solid (1·04 g.). This was crystallised from light petroleum (500 c.c.; b. p. 80—100°) and a faintly yellow product (total yield, 0·69 g.), m. p. 135—140°, was obtained [yield of this product, calculated on the amount of (III; R = CHO) which underwent change, 59%]. The pure *substance* separated from hot water in rhombic prisms, m. p. 145—146° (Found: C, 68·6; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

2 : 4-*Dimethoxy*-5-*allylstyryl Methyl Ketone* (X).—2-*O*-Methyl-5-allyl-β-resorcylaldehyde (0·4 g.) in acetone (40 c.c.) was methylated at the boiling point in the usual way with methyl sulphate (10 c.c.) and excess of 20% aqueous potassium hydroxide during 1 hour. After removal of the acetone by distillation the product was extracted with ether, and the extract shaken with alkali, dried, and distilled, leaving a crystalline solid (0·47 g.). It separated from light petroleum (b. p. 60—80°) at 0° in small yellow crystals, m. p. 76—77° (Found: C, 73·2; H, 7·5. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

2 : 4-*Dimethoxy*-3-*allylstyryl methyl ketone* (IX), prepared by methylation of 3-allyl-β-resorcylaldehyde in acetone as described in the previous case, separated from light petroleum (b. p. 40—60°) in small, very faintly yellow prisms, m. p. 45° (Found : C, 73·3; H, 7·2. $C_{12}H_{18}O_3$ requires C, 73·2; H, 7·3%).

4-*Methyl*-2-n-*propylresorcinol* (VII).—(A) 3-Allyl-β-resorcylaldehyde (1·5 g.) in alcohol (20 c.c.) was reduced at room temperature with hydrogen in presence of palladium chloride (0·13 g.). During 4 hours hydrogen corresponding to 3 molecules (500 c.c.) was absorbed, the first molecule (probably owing to the reduction of the allyl group) more rapidly than the other two. The filtered solution left an oil which solidified on scratching; it separated from light petroleum (b. p. 80—100°) in faintly pink needles, m. p. 96—97° (Found : C, 71·9; H, 8·4. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). The substance sublimed in colourless feathery needles on the water-bath, and its solution in dilute alcohol gave no coloration with ferric chloride. (B) 3-*n*-Propyl-β-resorcylaldehyde (VIII) (below) was catalytically reduced under the conditions described in experiment (A), two molecules of hydrogen being absorbed. The product, twice crystallised from light petroleum, formed needles, m. p. 96—97°, either alone or when mixed with the specimen prepared by method (A), and the two substances were identical in all properties.

3-n-*Propyl*-β-*resorcylaldehyde* (VIII).—2-*n*-Propylresorcinol (0·4 g.) (Baker and Lothian, *loc. cit.*; compare Nesmejanow and Sarewitsch, *Ber.*, 1935, **68**, 1478) in anhydrous ether (10 c.c.) containing liquid hydrogen cyanide (2 c.c.) was slowly saturated at 0° with dry hydrogen chloride. After 12 hours, an equal volume of dry ether was added, and the ether was decanted from the solid aldimine hydrochloride, which was then hydrolysed by heating with water (15 c.c.) for 20 minutes. The solid *aldehyde* separated on cooling and was recrystallised from boiling water (20 c.c.), forming colourless fibrous needles, m. p. 92—93° (Found : C, 66·3; H, 6·6. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). Its alcoholic solution gave a deep brown coloration with ferric chloride.

2-*Hydroxy*-5-*allyloxyacetophenone* (XI).—A mixture of 2 : 5-dihydroxyacetophenone (19 g.; 1 mol.), allyl bromide (16 g.; 1 mol.), and anhydrous potassium carbonate (25 g.) in acetone (50 c.c.) was refluxed and stirred on the water-bath for 9 hours. After dilution with water, the mixture was shaken with a large volume of ether, and the ethereal extract shaken twice with water and then with 20% aqueous sodium hydroxide (200 c.c.). The sodium salt of 2-hydroxy-5-allyloxyacetophenone at once separated as yellow crystalline plates, which were collected, washed with cold 20% sodium hydroxide solution, then with ether, and decomposed with dilute hydrochloric acid. The oily product rapidly solidified, and was collected, washed, and dried (17·5 g.); it separated from light petroleum (b. p. 40—60°) in large, thick, almost rectangular, pale yellow prisms, m. p. 59—60° (Found : C, 69·0; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). It dissolved in aqueous sodium hydroxide with a yellow colour, and gave an intense indigo-blue coloration with alcoholic ferric chloride. When warmed with copper acetate solution as in the preparation of the copper derivative of (I; R = Et) and subsequently shaken with chloroform, it gave a green solution of a copper derivative. The derivative was readily soluble in benzene and chloroform, giving green solutions, but it could not easily be separated from the parent substance (XI).

2 : 5-*Dihydroxy*-6-*allylacetophenone* (XII).—2-Hydroxy-5-allyloxyacetophenone (4 g.) was placed in an oil-bath at 180°, and the temperature raised during 35 minutes to 230°. After about 15 minutes, the slightly exothermic reaction caused the temperature of the melt to rise 4° higher than that of the oil-bath. The product solidified on cooling, and was collected (3·91 g.), crushed, and treated twice with boiling light petroleum (20 c.c.; b. p. 40—60°), the insoluble residue refluxed with carbon tetrachloride (150 c.c.), and the resulting solution filtered. It slowly deposited almost colourless plates, m. p. 105—106° (2·88 g.; 74% yield). Recrystallisation from a little benzene gave elongated rhombic plates, m. p. 107·5° (Found : C, 68·9; H, 6·2. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). With alcoholic ferric chloride it gave a green coloration, fading rapidly to yellow, and with aqueous ferric chloride a transient blue.

2 : 5-*Dimethoxy*-6-*allylacetophenone* (XV).—(A) 2 : 5-Dihydroxy-6-allylacetophenone was treated in acetone solution with much methyl sulphate and excess of 20% aqueous potassium hydroxide, finally on the water-bath for ½ hour. The methylated product was extracted with ether, and was isolated as a colourless oil, b. p. 164—165°/14 mm., $n_D^{13°}$ 1·534 (Found : C, 70·9; H, 7·4. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). (B) Methylation of 5-hydroxy-2-methoxy-6-allylacetophenone (below) in a similar manner gave a product, b. p. 164°/14 mm., $n_D^{13°}$ 1·535 (Found : C, 70·9; H, 7·2%). Neither specimen would yield a semicarbazone when treated with semicarbazide hydrochloride and sodium acetate in dilute alcohol under a wide variety

of conditions (compare formation of semicarbazone of 3-allylresacetophenone dimethyl ether, below).

2 : 5-*Dimethoxy-6-allylphenyl Styryl Ketone.*—Specimens (A) and (B) of 2 : 5-dimethoxy-6-allylacetophenone (above) were separately treated in alcoholic solution with benzaldehyde (1 equiv.) and a drop of 10% aqueous sodium hydroxide and left over-night. The diluted solutions yielded to ether yellow oils, which solidified and then crystallised (separately) from light petroleum (b. p. 60—80°) in pale yellow, stout, rectangular prisms, m. p. and mixed m. p. 75° (Found: C, 78·1; H, 6·5. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·4%).

2-*Methoxy-5-allyloxyacetophenone* (XIII).—2-Hydroxy-5-allyloxyacetophenone was methylated in acetone solution by the alternate addition of methyl sulphate and excess of 20% aqueous potassium hydroxide, with final heating on the water-bath for ½ hour. The methylated product was extracted with ether from the diluted liquid, and obtained as a colourless oil, b. p. 166°/13 mm., $n_D^{11°}$ 1·548 (Found: C, 69·8; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

5-*Hydroxy-2-methoxy-6-allylacetophenone* (XIV).—2-Methoxy-5-allyloxyacetophenone (2 g.) was placed in an oil-bath at 220°, the temperature of which was raised to 230° during 20 minutes. The maximum excess temperature of the melt over that of the bath was 1·5°. The solid product was dissolved in dilute aqueous sodium hydroxide, and, after the solution had been shaken with ether to remove the unchanged allyl ether, was reprecipitated by the addition of hydrochloric acid at 0°, collected, washed, and dried (1·57 g.). Crystallisation from carbon tetrachloride gave colourless rhombic prisms (1·40 g.), m. p. 104° (Found in material dried in a vacuum at 100°: C, 69·6; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). By working up the mother-liquors, a total of 1·48 g. of pure 5-*hydroxy-2-methoxy-4-allylacetophenone* was obtained, equivalent to 94% of the theoretical yield from the alkali-soluble product of the rearrangement.

The *semicarbazone* of 3-allylresacetophenone dimethyl ether, prepared from 3-allylresacetophenone dimethyl ether (Baker and Lothian, *loc. cit.*) in the usual manner, separated from benzene in prismatic needles, m. p. 159—160° (Found: N, 15·0. $C_{14}H_{19}O_3N_3$ requires N, 15·2%).

4-*Ethylresorcinol Diacetate.*—4-Ethylresorcinol was boiled with an excess of acetic anhydride for 2 hours, the mixture shaken with water and extracted with ether, and the extracts shaken with aqueous sodium bicarbonate in excess, dried, and distilled, giving a colourless liquid, b. p. 162°/14 mm. (Found: C, 64·8; H, 6·4. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). This compound is merely mentioned by Rosenmund, Buchwald, and Deligiannis (*Arch. Pharm.*, **1933**, **271**, 344).

4-*Ethylresorcinol diallyl ether*, produced as the non-phenolic product when 4-ethylresorcinol was allylated in acetone solution with allyl bromide and potassium carbonate under the usual conditions, was a colourless oil, b. p. 146°/10 mm. (Found: C, 77·1; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%).

Ethyl 4-O-*Allyl*-β-*resorcylate.*—Ethyl β-resorcylate (36·4 g.), allyl bromide (25 g.), acetone (100 c.c.), and potassium carbonate were stirred and boiled under reflux for 8 hours. After dilution with water, the solution yielded to ether a low-melting solid (42 g.), which separated from alcohol (120 c.c.) in prismatic needles (20 g.), m. p. 42° (Found: C, 65·0; H, 6·2. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%). The alcoholic solution gave an intense purplish-red colour with ferric chloride.

4-O-*Allyl*-β-*resorcylic acid*, prepared by hydrolysis of the preceding ester with 10% sodium hydroxide solution, separated from 50% alcohol in prismatic needles, m. p. 155—156° (Found: C, 61·5; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·1%). The ferric chloride reaction is similar to that given by the ester.

4-*Nitroresorcinol.*—The potassium salt of 4-nitrosoresorcinol was prepared, according to the directions of Henrich (*Ber.*, **1902**, **35**, 4192), from resorcinol, alcoholic potassium hydroxide, and amyl nitrite. We were unable to convert the substance into 4-nitroresorcinol by oxidation with hydrogen peroxide under the conditions described by Borsche and Berkhout (*Annalen*, **1903**, **330**, 106) and could only obtain traces of the desired product by the method of Gilbert, Laxton, and Prideaux (J., 1927, 2299). The following method gives poor, but reproducible yields. A solution of the freshly prepared potassium salt of 4-nitrosoresorcinol (10 g.) in a mixture of 6% hydrogen peroxide (30 c.c.) and perhydrol (10 c.c.) was cautiously warmed until signs of reaction became apparent, and then placed in a vessel of cold water. A violent reaction occurred, which was allowed to continue for 5 minutes with occasional warming; the solution was cooled, acidified with 2*N*-sulphuric acid (10 c.c.), and extracted five times with chloroform (total volume 500 c.c.; 4-nitrosoresorcinol is insoluble in chloroform); the extracts were dried over sodium sulphate and distilled, leaving a bright yellow solid (0·5 g.). This separated from

hot water in needles of the hemi-hydrate; after dehydration at 70° it had m. p. 115°. The yield is not correspondingly increased by working with larger quantities.

4-*Nitroresorcinol* 1-O-*Allyl Ether*.—Anhydrous 4-nitroresorcinol (10 g.) in acetone (50 c.c.) was heated and stirred under reflux for 12 hours with allyl bromide (10 g.) and potassium carbonate (20 g.). After removal of most of the acetone and acidification with dilute hydrochloric acid, the products were extracted with ether, the extracts shaken with 15% sodium hydroxide solution, and the very sparingly soluble sodium salt of 4-nitroresorcinol 1-*O*-allyl ether collected on a sintered glass funnel and washed with a little sodium hydroxide solution and then with more ether. The sodium salt yielded the free *compound* as a pale yellow oil, b. p. 157—158°/10 mm. (Found : C, 55·9; H, 4·8. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

4-*Nitro*-6 (or 2)-*allylresorcinol*.—4-Nitroresorcinol 1-*O*-allyl ether (2·5 g.) was heated at 185° for 50 minutes, and the product shaken with 10% sodium hydroxide solution. The insoluble sodium salt was collected, washed with ether, and decomposed by the addition of acid, yielding unchanged 4-nitroresorcinol 1-*O*-allyl ether (1·24 g.). The alkaline filtrate yielded to ether a solid (0·43 g.), m. p. 67—77°, which after two crystallisations from light petroleum (b. p. 40—60°) formed yellow prisms (0·32 g.; 26% yield on rearranged product), m. p. 85·5° (Found : C, 55·6; H, 4·8. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

Nitroquinol Diallyl Ether.—This compound appears to be the sole product of the allylation of nitroquinol in acetone solution, although monoallylation may be effected in alcoholic solution (succeeding preparation). Nitroquinol (20 g.) in acetone (100 c.c.) was stirred under reflux for 6 hours with allyl bromide (15 g.; 1 mol.) and potassium carbonate (30 g.). Most of the acetone was removed by distillation, and the diluted solution was extracted with ether. Pure, unchanged nitroquinol was removed from the extract by shaking with alkali, and after evaporation of the ether the remaining oil solidified at 0°. The product separated from light petroleum (b. p. 40—60°) at 0° in light yellow needles, m. p. 22° (Found : C, 61·2; H, 5·6. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·4%).

2-*Nitroquinol* 4-O-*Allyl Ether*.—Nitroquinol [8 g.; conveniently prepared by demethylation of its dimethyl ether by boiling with 10 times its weight of a mixture of equal volumes of glacial acetic acid and hydrobromic acid (*d* 1·5) for 12 hours, and extracting the carefully neutralised solution with ether] in alcohol (50 c.c.) was refluxed for 6 hours with allyl bromide (6·2 g.; 1 mol.) and an alcoholic solution of sodium ethoxide (from 1·18 g. of sodium; 1 mol.). The diluted solution was made strongly alkaline, extracted with ether, then acidified, and subjected to steam distillation. The 2-*nitroquinol* 4-O-*allyl ether* (1 g.) collected from the distillate crystallised from light petroleum (b. p. 40—60°) in masses of fine, bright yellow needles, m. p. 48° (Found : C, 55·8; H, 4·5. $C_9H_9O_4N$ requires C, 55·4; H, 4·6%).

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, December 20th*, 1935.]