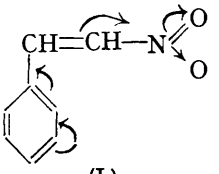
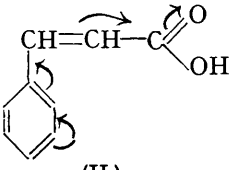
366. *Hydrolysis of Arylsulphuric Acids. Part IV.* (a) *Conjugation between the Benzene Nucleus and Unsaturated Side Chains.* (b) *Steric Effects and the Influence of Alkyl Groups.*

By G. Norman Burkhardt, Charles Horrex, and Doreen I. Jenkins.

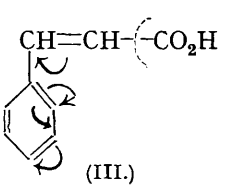
(a) The fact that cinnamic acid and ω-nitrostyrene give *op*-derivatives on substitution has presented a problem in the application of polar and electronic theories of organic reactions in that the normally *m*-directive carboxy- and nitro-groups might be expected to exercise their influence through the double bond conjugated with the nucleus (I, II).



(I.)



(II.)



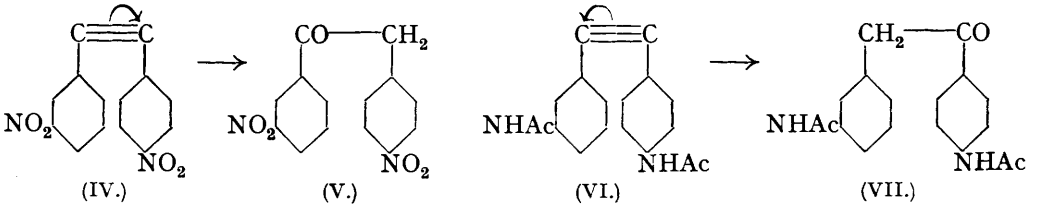
(III.)

Two explanations have been discussed. Considering the observation that ω-nitrostyrene gives less *m*-derivative on nitration than does ω-nitroethylbenzene, Ingold (*Ann. Reports*, 1926, **23**, 132) took the view that the ethylene bond efficiently damps the effect of the terminal nitro-groups. Baker and Wilson (J., 1927, 842) developed this in the light of further orientation results, and concluded that the *op*-directive influence of the ·CH:CH·NO_2 group arises in the union of the first side-chain carbon atom with the nucleus, in the same way as in toluene. However, the ethylene bond is known to trasmit the electron-attractive character of these *m*-directive groups to the β-position in the αβ-double bonds. Many of the addition reactions of the ethylenic bond in cinnamic acid, benzylidenemalonic acid derivatives, and ω-nitrostyrene show this clearly, and the fact that in these substances the double bond is less reactive than in corresponding aliphatic compounds is usually accounted for by assuming conjugation between the side chain and the nucleus. This must involve some transmission of the effect under consideration (cf. Ashworth and Burkhardt, J., 1928, 1791; Ingold, *Ann. Reports*, 1928, **25**, 147). On the other hand, however, the large amount of evidence available concerning substitution in the diphenyl series gives practically no indication of such an effect passing from one nucleus to the other, and this has been taken to support the view that conjugation between the nuclei is very small indeed. By analogy, this suggests a similar lack of interaction between unsaturated side chains and aromatic nuclei.

The second explanation (Robinson, Inst. Chem. Lectures, 1932, 49) is that if the ethylenic bond polarises free from the influence of the terminal *m*-directive groups, it will do so in the manner which leads to *op*-substitution in styrene (III). This will lead to strong activation of the *o*- and *p*-positions in reactions with the ordinary electron-seeking substituting agents, whereas the other phase will lead to deactivation of all positions. Therefore, even very infrequent independent (styrene) polarisations of the ethylenic bond will lead to high percentages of *op*-products owing to preferential attack on this phase. This explanation accounts for the facts concerning substitution in ω-substituted derivatives of styrene and can be applied *mutatis mutandis* to substitution in the diphenyl series, but it has been open to criticism as a special explanation for which little positive evidence was available. Essentially, however, it depends on the view that in substitution reactions the independently (styrene) activated phase will be preferentially attacked, and it involves the view that, in reactions where this does not apply, the electron-attractive effect of a terminal *m*-directive group should be detected in so far as it is transmitted.

Previous work has provided some examples indicative of the transmission of similar effects in the opposite direction (*i.e.*, from the nucleus to the ethylenic side chain), the significance of which does not seem to have been generally recognised. Harrison (J., 1926, 1932) showed that 3 : 4′-dinitro- and 3 : 4′-diacetamido-tolan, (IV) and (VI), were

hydrated in opposite directions by sulphuric acid, giving the ketones (V) and (VII) respectively.



(IV.) (V.) (VI.) (VII.)

The same effect is shown in the rates of hydrolysis of substituted benzoic, phenylacetic, phenylpropionic, and cinnamic esters (Table I):

TABLE I.

Velocity constants ($\times 10^4$) *at* 30° *for the alkaline hydrolysis of esters* (Kindler, *Annalen*, 1927, **452**, 90).

Acid.	*p*-NO_2.	*m*-NO_2.	*m*-Cl.	*p*-Cl.	*m*-OMe.	H.	*m*-Me.	*p*-Me.	*p*-OMe.
Benzoic	5090	3110	363	212	59	49	35	23	10·5
Phenylacetic	4570	—	—	1620	—	636	—	585	580
Phenylpropionic	—	—	—	516	—	343	—	—	288
Cinnamic	1037	798	—	215	—	106	—	75·4	44·4

The action of substituents is at a maximum in the benzoic esters and is suppressed by the introduction of saturated carbon atoms, but much less so by the unsaturated chain in the cinnamic series. This is perhaps most significant in the case of the *p*-methoxy-group, where the deactivating primary interior or mesomeric effect is characteristic.

The dissociation constants of a suitable group of carboxylic acids show a similar relationship, and this indicates specifically the transmission of the permanent effects:

Dissociation constants ($\times 10^5$) *of carboxylic acids at* 25°.

Benzoic	6·46	Phenylacetic	5·03	Cinnamic	3·6
Anisic	3·43	*p*-Methoxyphenylacetic	4·45	*p*-Methoxycinnamic	2·0
Ratio	1·88	Ratio	1·13	Ratio	1·8

The influence of methoxyl in depressing the dissociation constants is more damped by the one saturated carbon atom of the side chain of phenylacetic acid than by the unsaturated cinnamic system. The variations in these cases are, however, small in comparison with possible, though not probable, errors.

As has been indicated above, evidence of the transmission of such effects as these from side chains to the nucleus has been lacking. Browne and Dyson (J., 1934, 178) found the following velocity constants for the reaction of *iso*thiocyano-groups with ethyl alcohol at 78·5° (time in minutes):

	k.		*k*.
p-$SCN\cdot C_6H_4\cdot CO_2Et$	4·13	*p*-$SCN\cdot C_6H_4\cdot CH_2\cdot CO_2Et$	0·74
m-$SCN\cdot C_6H_4\cdot CO_2Et$	3·07	$SCN\cdot C_6H_5$	0·5
p-$SCN\cdot C_6H_4\cdot CH{:}CH\cdot CO_2Et$	2·26	*p*-$SCN\cdot C_6H_4\cdot [CH_2]_2\cdot CO_2Et$	0·33

This reaction is, in general, accelerated by low electron availability, though, if this is so, some of the other substituents examined apparently do not behave normally. Browne and Dyson ascribe the acceleration in cinnamic derivatives to the unsaturated side chain, but these results might be taken to show a quite efficient transmission of the electron-attractive effect of the carboxyl to the nucleus.

The hydrolysis of arylsulphuric acids has been shown to be a normal reaction of the type accelerated by electron recession (Burkhardt, Ford, and Singleton, this vol., p. 17). The results previously obtained have now been extended to include groups containing carbonyl in the *m*- and *p*-positions relative to the sulphate group, both directly attached to the nucleus and separated from it by saturated and unsaturated side chains. The results (Table II, where *k* for 78·7° is given in mols./l./sec.) appear to show the transmission into the aromatic

nucleus, of the electron-attractive effect of the carboxyl group in cinnamic acid. The rate of hydrolysis of the sulphate group is much greater when it is *p*- to the cinnamic side chain than when in the *m*-position, as is found with typical *m*-directive substituents—indeed, in both the *p*- and the *m*-series, the cinnamic side chain appears as the least effective of the groups containing carbonyl so placed that conjugation with the nucleus is possible.

TABLE II.

Substituent.	100 *k*.	Substituent.	100 *k*.	Substituent.	100 *k*.
p-CHO	1·01	*m*-CHO	0·453	(Unsubstituted)	0·335
p-CO·CH$_3$	0·772	*m*-CO$_2$H	0·440	*m*-CH$_2$·CH$_2$·CO$_2$H	0·292
p-CO$_2$H	0·657	*m*-CO·CH$_3$	0·418	*p*-CH$_2$·CH$_2$·CO$_2$H	0·280
p-CH:CH·CO$_2$H	0·585	*m*-CH:CH·CO$_2$H	0·350	*p*-CH$_2$·CH$_3$	0·248
o-CHO	0·580				

The propionic side chain behaves quite differently : the *m*-substituted acid is hydrolysed slightly faster than the *p*-isomeride (the difference is about equal to the probable experimental error) and both values lie between those of the unsubstituted phenylsulphate and its *p*-ethyl derivative. Hence, this side chain behaves, as might be expected, like an *op*-directive (alkyl) substituent less powerful than the ethyl group. On this basis, the constant for the *m*-compound is further from the value for the unsubstituted compound than would have been anticipated.

To establish the true extent to which the influence of the carbonyl group is responsible for the results obtained with the sulphates of the hydroxycinnamic acids, it will be necessary to eliminate the effect of the ethylenic system itself by examining other derivatives of the hydroxystyrenes. The identity of the rates for the sulphates of 3- and 4-hydroxydiphenyl, however, confirms the view that the unsaturation of the side chain cannot alone be responsible for effects of the magnitude observed.

The above discussion has been expressed in terms which do not involve the most detailed analysis of the effects involved, and particularly without considering the contribution which should be assigned to inductive effects. A more detailed treatment will be necessary and possible in considering the influence of heteropolar groups.

The Influence of Mesomeric Displacements in Unsaturated Systems on the Properties of Attached Saturated Chains.—Nuclear substituents fall in the same sequence, when they are arranged according to their influence on the dissociation constants of carboxylic acids or on the rates of hydrolysis of carboxylic esters, whether one considers benzoic, phenylacetic, phenylpropionic, or cinnamic acids or their esters (compare Table I). In particular, the *p*-methoxyl group lowers the electron availablity, at the end of attached saturated side chains, in spite of its electron-attractive field and inductive effects. It is clear, therefore, that the influence of changes of electron distribution set up in an aromatic nucleus by mesomeric effects can be transmitted along a saturated side chain, and that the presence, next to the nucleus, of an unsaturated hetero-atom, such as sulphur, is not necessary for the operation of this effect (compare Bennett, *Chem. and Ind.*, 1932, **10**, 776). In addition to the examples quoted above, the effect of terminal methyl groups on the dissociation constants of unsaturated aliphatic acids (Ives, Linstead, and Riley, J., 1933, 561) is an example of a similar effect initiated in an ethylenic system.

The aldehydo-, carboxy-, and acetyl groups directly attached to the nucleus fall, as a series, in their anticipated position between the nitro-group and hydrogen. In the *p*-position these groups lie in the sequence of diminishing additive power of the carbonyl (CHO>CO·CH$_3$>CO$_2$H), whereas in the *m*-position the carboxyl group lies between the other two. This is accounted for by the greater relative influence of the effective dipole on the *m*-position (compare Baker and Ingold, J., 1927, 832; Cooper and Ingold, *ibid.*, p. 836).

(b) *Steric Effects and the Influence of Alkyl Groups.*—In Part I it was observed that the hydrolysis of the phenylsulphuric acids resembles that of the benzyl chlorides in being very insensitive to steric effects. The extended results given in Table III (relating to a temperature of 78·7°) show that *o*-substituents containing two atoms or more (other than hydrogen) do exert a definite inhibitory effect in virtue of their position. The fact that larger groups

show such steric influences does not, however, modify the conclusions concerning the mechanism of the hydrolysis which were derived from the smallness of these effects, especially in the case of chlorine and methyl substituents.

TABLE III.

Substituent	*o*-Cl	*p*-Cl	*o*-Me	*p*-Me	*m*-Me	*o*-Et	*p*-Et	*o*-Pr$^{\beta}$	*o*-Ph	*p*-Ph	*m*-Ph
100 *k*	0·442	0·362	0·272	0·238	0·320	0·137	0·248	0·15*	0·245	0·38*	0·38*

Substituent (or aryl group)	*o*-CHO	*p*-CHO	*m*-CHO	*o*-NO_2	*p*-NO_2	α-$C_{10}H_7$	β-$C_{10}H_7$	Thymyl
100 *k*	0·580	1·01	0·453	0·88	1·20	0·245	0·382	0·146

* These values are regarded as more uncertain than the others, for only small amounts of *o-iso*-propylphenol were available, and potassium *m*- and *p*-phenylphenylsulphate and the corresponding phenols are difficultly soluble in water. The anomaly of the *o*-methoxy-group was noted in Part I.

The phenylsulphates containing alkyl substituents were examined in the first instance because this reaction was one which might be expected to show the decrease of electron-repulsive character in ascending the homologous series of alkyl groups that had been deduced on theoretical grounds by Burkhardt and Evans (*Mem. Manchester Lit. Phil. Soc.*, **1933**, **77**, 37). This effect has now been observed by Baker and Nathan (J., 1935, 1844), and by Baker, Nathan, and Shoppee (*ibid.*, p. 1847) in two other reactions. From these results, Baker and Nathan have developed views on the genesis of these effects similar, at least in outline, to those referred to above (cf. *Chem. and Ind.*, **1936**, **55**, 158). The following quotation from Burkhardt and Evans (*loc. cit.*) indicates the ideas relevant to the present discussion :

"$-CH_3$ *Group*.—As far as the (primary interior) effect which we are considering is concerned, this group falls into line with the other *op*-directing groups, since as a condensed atom group it simulates the structure of the halogens, and all the electrons (except the 1*s* electrons of the carbon) are making up the outer electronic shell of the group. The methyl group cannot, of course, take part in full electromeric change to quinonoid forms. The replacement of the hydrogen in $-CH_3$ by other groups not only reduces the nuclear charge by destroying the condensed atom system but also removes to some extent the electrons which were available and taking part in the bond when the group resembled the fluorine structure. Such a decrease in availability of electrons may contribute to the apparent decrease in *op*-directing power of substituted methyl groups (compare Le Fèvre, *Nature*, **1933**, **131**, 655, on the relative effects of methyl and *tert.*-butyl)."

The rate of hydrolysis of potassium *p*-ethylphenylsulphate is greater than that of the *p*-tolylsulphate, indicating that the ethyl substituent is less electron-repulsive than methyl, as was predicted. The same effect would also account for the fact that the *o-iso*propylphenylsulphate is more rapidly hydrolysed than the *o*-ethyl derivative, but with most of the arylsulphates containing *o*-alkyl groups steric factors clearly overpower any effect of this type. As this particular reaction is only slightly inhibited by *o*-groups, it must be concluded that steric influences are mainly responsible for the results obtained in the nitration of *p*-alkyltoluenes, as Le Fèvre suggested, and that the localisation of electron distribution in the higher alkyl groups plays only a minor part in reactions involving the *o*-position.

EXPERIMENTAL.

Velocity Measurements.—The hydrolyses were carried out in electrically controlled thermostats at 78·7° (± 0·02°) and 48·7° (± 0·02°). The procedure was similar to that used previously (Burkhardt, Ford, and Singleton, *loc. cit.*), with the following modifications. Pipettes were used having jets directly on the ends of the bulbs so that the bulbs were entirely within the reaction flasks, and the emergent stem was a minimum when the meniscus was set. The pipettes were calibrated at the temperature of the reaction. The 10 c.c. samples removed for analysis were pipetted into 15 c.c. of *N*/10-alkali, standardised in control experiments on each occasion with the same indicator. The excess alkali was titrated with *N*/20-hydrochloric acid, bromophenol-blue being used as indicator in most cases, and all the phenol being assumed to be free at the end-point. With the carboxyphenylsulphates, bromothymol-blue was used, and with the

*iso*propylphenol and cinnamic derivatives, phenol-red. In all cases the end-points were satisfactory and were controlled by matching. With the carboxylic acid derivatives the initial titrations corresponded with the total acidity due to the hydrochloric acid and the carboxyl group of the sulphate used. The procedure was further tested by titrating *p*-hydroxybenzoic acid with alkali under similar conditions (cf. Kolthoff, *J. Amer. Chem. Soc.*, 1935, **57**, 973). As the total acid content obtained from the titrations included the carboxyl group, the amount of this, deduced from the concentration of the solution used initially, was deducted from the total found in each sample to give the hydrochloric acid and potassium hydrogen sulphate which were assumed to be the only effective sources of hydrogen ion for catalysis. The hydrolysis of potassium *p*-aminophenylsulphate could not be followed by a similar titration method, the amino-group being too strongly basic.

Materials.—Phenols for conversion into sulphates were purchased (except those indicated below), and the m. p. or b. p. checked. *o*- and *p*-Hydroxyacetophenones were made by Freudenberg and Orthner's method (*Ber.*, 1922, **55**, 1749) for the *o*-isomeride, which was separated by steam distillation (b. p. 206—210°). The *p*-isomeride was recrystallised from water and decolorised in benzene solution by charcoal (m. p. 108° from benzene).

m-*Hydroxyacetophenone.* Acetophenone was nitrated (Corson and Hagen, "Organic Syntheses," Vol. 10). *m*-Nitroacetophenone was reduced by stannous chloride in aqueous-alcoholic hydrogen chloride, giving *m*-aminoacetophenone (m. p. 99° after one crystallisation; yield 60%). This method of reduction proved more satisfactory than those of Mayer and English (*Annalen*, 1918, **417**, 82) or Rupe, Braun, and von Zembruski (*Ber.*, 1901, **34**, 3522). The *m*-aminoacetophenone was diazotised, and the diazonium salt decomposed by running the solution into boiling 6*N*-sulphuric acid.

m- and *p*-Hydroxycinnamic acids, m. p. 191° and 206° respectively, prepared by the Perkin reaction (Sonn, *Ber.*, 1913, **46**, 4050; Reiche, *Ber.*, 1889, **22**, 2356), were reduced by sodium amalgam to *m*- and *p*-hydroxy-β-phenylpropionic acids, m. p. 111° and 129° respectively (Tiemann and Ludwig, *Ber.*, 1882, **15**, 205).

o- and *p*-Ethylphenols were prepared by Clemmensen reduction of *o*- and *p*-hydroxyacetophenones and purified by distillation, the *p*-isomeride being once distilled in steam; b. p. 198—200° and 214—216° respectively.

o-iso*Propylphenol.* Salicylic acid was methylated and esterified by the action of methyl sulphate and alkali. The subsequent treatment was based on the method outlined by Béhal and Tiffeneau (*Bull. Soc. chim.*, 1908, **3**, 316). The methyl ether of methyl salicylate in ether was run into methylmagnesium iodide (>4 mols.) in ether, and the solution refluxed for 4 hours. The *o-iso*propenylphenyl methyl ether was isolated in the usual way and purified by distillation under reduced pressure (b. p. 81—82°/15 mm.); it (25 g.) was then reduced in amyl alcohol (250 c.c.) with sodium (25 g.). The product, which decolorised cold dilute permanganate only very slowly (contrast the mixed product obtained by Béhal and Tiffeneau, using ethyl alcohol in the reduction), was steam distilled, extracted, dried, and distilled, first under reduced and then under atmospheric pressure (7 g.; b. p. 194—197°). It was demethylated by boiling with hydriodic acid for 12 hours, and the *o-iso*propylphenol isolated by dilution, extraction, solution in alkali, reprecipitation with carbon dioxide, and fractionation; b. p. 210—214°.

An alternative method was also examined (compare Niederl and Natelson, *J. Amer. Chem. Soc.*, 1931, **53**, 1372): phenyl *iso*propyl ether (34 g.) was heated (125—130°) for 5 hours with 125 c.c. of a 15% solution of sulphuric acid in glacial acetic acid, and then kept overnight. The phenolic products, reprecipitated from alkaline solution with acid, were fractionated under 13—14 mm., giving fractions b. p. 80—100° (8 c.c.) and 170—180° (5 c.c.). Refractionation of the first fraction gave a product corresponding with that obtained by the first method. The second fraction solidified, and was recrystallised from aqueous alcohol; m. p. 121—122° (unidentified).

2-*Hydroxydiphenyl.* A commercial specimen was dissolved in sodium hydroxide, and the solution extracted with ether. The phenol was liberated by carbon dioxide, taken up in ether, and obtained by evaporation. It crystallised from boiling ligroin (b. p. 40—60°) (charcoal); m. p. 58—59°.

3-Nitrodiphenyl was prepared from diazotised *m*-nitroaniline and benzene by the method of Blakey and Scarborough (J., 1927, 3000), except that it was isolated from the tarry crude product by distillation in superheated steam (170° on entering the flask) and purified by crystallisation from alcohol, m. p. 62°. This was more convenient than ligroin extraction (Blakey and Scarborough) and better than distillation under 2—3 mm., which resulted in considerable loss by decomposition.

3-Aminodiphenyl, obtained by reducing the nitrodiphenyl as for the 4-isomeride, was shaken in ethereal solution with dilute sulphuric acid; the sulphate which separated was recrystallised, decomposed with alkali, and the amine crystallised from ether; m. p. 30°.

3-Hydroxydiphenyl was obtained from the diazotised amino-derivative as for the 4-isomeride. The tarry product was extracted with ligroin, the solution nearly decolorised with charcoal, and the product obtained on evaporation recrystallised from ligroin (b. p. 40—60°); m. p. 75°.

4-Nitrodiphenyl, m. p. 113—114°, prepared by nitration of diphenyl (Luddens, *Ber.*, 1875, **8**, 871) and recrystallised from glacial acetic acid, was reduced to the amino-derivative by stannous chloride in aqueous-alcoholic hydrochloric acid (Schlenk, *Annalen*, 1909, **368**, 303), and the amine (17 g.) was converted into 4-hydroxydiphenyl by adding the solution of the diazonium derivative to hot sulphuric acid (750 c.c.; 30%). The tarry product was distilled with superheated steam (150°), and the phenol recrystallised from 20% aqueous alcohol (m. p. 162—163°).

4-Hydroxydiphenyl was obtained more quickly by diazotising aniline (34 g.) in dilute sulphuric acid (2 : 1, by wt.) and adding the resulting solution in portions to phenol (170 g.) heated on a steam-bath (Norris, MacIntire, and Corse, *Amer. Chem. J.*, 1903, **29**, 120; Raiford and Colbert, *J. Amer. Chem. Soc.*, 1925, **47**, 1454). The mixture of 2- and 4-hydroxydiphenyls, isolated by distillation in superheated steam, was separated by treatment with ligroin (b. p. 60—80°), and the residue after extraction was crystallised from 20% aqueous alcohol; 12 g., m. p. 162—163°.

Preparation of the potassium arylsulphates. All were prepared by the method of Burkhardt and Lapworth (J., 1926, 684), apart from the modifications indicated below.

Potassium o-, m-, *and* p-*aldehydophenylsulphates.* Pyridine was used instead of dimethylaniline, and potassium carbonate instead of the hydroxide.

Potassium m- *and* p-*acetylphenylsulphates.* Pyridine was again used as the base, and excess of it as a solvent to replace carbon disulphide, in which the phenols were too insoluble. Potassium carbonate replaced the hydroxide.

Potassium m-*carboxyphenylsulphate.* Chlorosulphonic acid (2·2 mols.), *m*-hydroxybenzoic acid (1 mol.), and dimethylaniline (5 mols.) were used to allow for the action of chlorosulphonic acid with the carboxyl group to give the mixed anhydride, which was hydrolysed by alkali in the extraction. Unchanged *m*-hydroxybenzoic acid was extracted by ether from the aqueous extract after acidification (controlled by indicator) below 5°. The aqueous solution was made alkaline, evaporated to small bulk, potassium sulphate and chloride removed, and monopotassium *m*-carboxyphenylsulphate precipitated together with some potassium sulphite by passing sulphur dioxide through the solution. The required product was extracted in methyl alcohol and crystallised.

Potassium p-*carboxyphenylsulphate.* The anhydrous dipotassium salt of *p*-hydroxybenzoic acid was used instead of the free phenol. It was prepared by evaporating a solution containing equivalent quantities of potassium hydroxide and the acid, and dried by means of benzene distillation and exposure in a vacuum desiccator. Excess chlorosulphonic acid was used to allow for small amounts of water, and the preparation continued as for the *m*-isomeride; 30% of *p*-hydroxybenzoic acid was recovered unchanged. The dipotassium salt of the product is relatively insoluble, so that only small quantities of the required mono-potassium salt could be obtained by precipitation with sulphur dioxide.

Potassium salts of the sulphates of m- *and* p-*hydroxy-cinnamic and* -β-*phenylpropionic acids.* As for potassium *m*-carboxyphenylsulphate, except that the hydroxy-acid was added in solution in excess of pyridine (3 mols. at least), which was used as the base throughout.

Purification of the potassium arylsulphates was generally effected by extraction from the crude product with methyl alcohol, followed by recrystallisation from this solvent and from water. The *p*-aldehydo- and *p*-acetyl-salts were separated from inorganic matter by extraction with methyl alcohol, and recrystallised several times from water.

With the *o*- and *m*-aldehydo-acid and *m*-acetyl-salts, which were too soluble to separate from solution without a large amount of inorganic material, the latter was first precipitated by the addition of hot ethyl alcohol to the hot concentrated solution. The mother-liquor was then evaporated, and the product recrystallised from ethyl alcohol. Of the potassium carboxyphenylsulphates, the *m*- was extracted with 75% aqueous acetone and recrystallised from methyl alcohol, whereas the *p*-isomeride, which was hydrolysed in extraction with aqueous acetone, was extracted and crystallised from methyl alcohol. The product contained a trace of potassium chloride.

The sulphates obtained from *m*- and *p*-hydroxycinnamic acids were crystallised from 75%

methyl alcohol, and for those from *m*- and *p*-hydroxy-β-phenylpropionic acids absolute methyl alcohol was used. The *m*-derivatives contained small percentages (2%) of dipotassium salts which had solubilities too close to those of the monopotassium salts for complete separation. Allowance was made for this in estimating the initial acidity of the solutions used in the hydrolysis.

The isomeric potassium diphenylsulphates were recrystallised several times from 50% methyl alcohol.

All products were tested for inorganic sulphate and chloride, and for the free phenol when possible, and the potassium was determined quantitatively. Except those for the carboxy-derivatives indicated above, all the results gave the theoretical molecular weights within 0·2—0·9%. In cases where contamination with potassium carbonate was troublesome in the purification, this was converted nearly completely into potassium sulphate before the potassium arylsulphate was taken into the organic solvent used in the purification.

THE UNIVERSITY, MANCHESTER. [*Received, May 5th*, 1936.]