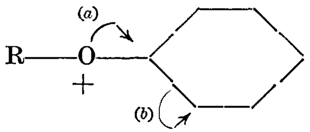
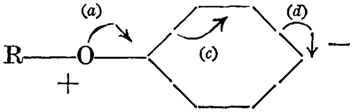
LII.—*The Relative Directive Powers of Groups of the Forms* RO *and* RR′N *in Aromatic Substitution. Part IV. A Discussion of the Observations Recorded in Parts I, II, and III.*

By JAMES ALLAN, ALBERT EDWARD OXFORD, ROBERT ROBINSON, and JOHN CHARLES SMITH.

IN order to avoid misconception as to the point of view adopted as a working hypothesis in this series of memoirs, a brief discussion of the fundamental principles is necessary.

It is recognised that certain ions, for example, those from sodium chloride, exhibit a high affinity for their charge and are relatively inert in the matter of co-valency formation, whereas other ions, for example, those from hydrogen cyanide or benzenediazonium hydroxide, have an intrinsic lower affinity for their charge and are active in the production of new bindings by co-valency. In effect, the former class are chemically inactive, the latter class active and, following Abegg and Bodländer, Kauffmann and Briggs, we can recognise in the two types diffuse and intense valency fields respectively. Lapworth has recently contributed a valuable classification of reagents as *anionoid* or *kationoid* according as they behave in the same way as active negative or positive ions (Paper read at the Manchester Literary and Philosophical Society on March 3, 1925; see abstract, *Nature*, **115**, 625). Ethylene, butadiene and benzene are anionoid, their *active* free valency has a negative polar character, and it is obvious that the ethers and amines are even more definitely anionoid. The systems which one of us has called *crotenoid* (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456) are strongly anionoid, the natural character of the unsaturated carbon being reinforced by direct union with an *onium* element. Lapworth points out that, when ethylene polarises, the implication is that the unsaturated carbon with a positive charge is in the more natural or stable condition and is surrounded by a diffuse field. The active unsaturated carbon with a negative charge is in a less natural condition, and this is justly held to be related to the observation that, except C_2H,* no hydrocarbon radicals have been observed to occur with a negative charge in Thomson's vacuum tube experiments. Independent of these acute comparisons, the development of the theory of crotenoid systems (Decker, *Ber.*, 1905, **38**, 2893; Hamilton and Robinson, J., 1916, **109**, 1029; Robinson, *ibid.*, p. 1038; *Mem. Manchester Phil. Soc.*, 1920, **64**, 4; Robinson and Robinson, J., 1917, **111**, 958; 1918, **113**, 640; Kermack and Robinson, J., 1922, **121**, 427) required the assumption that the reactive carbon atoms in phenols and amines and their derivatives acquire a negative charge in the course of polarisation, the postulated precedent of all reactions. In the case of a phenol ether the mechanism of activation is represented by the annexed expressions.

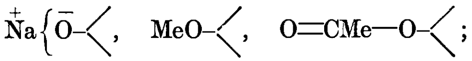




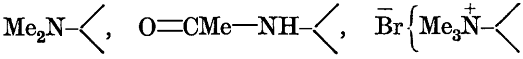
The oxygen, by means of its free electrons, increases its co-valency with the ring C_α (process *a*). C_α recovers its normal co-valency by giving up correspondingly electrons to C_β (process *b*) (*o*-substitution) or by relinquishing $C_\alpha C_\beta$ co-valency electrons to $C_\beta C_\gamma$ (process *c*). C_γ must then relinquish $C_\gamma C_\delta$ co-valency electrons to the sole use of C_δ (process *d*) (*p*-substitution). In the activated form the oxygen is positively charged and is exhibiting oxonium character, a *rôle* in which it far more closely resembles, in its general stability, the satisfied ions ($\overset{-}{\mathrm{Cl}}$, $\overset{+}{\mathrm{Na}}$) than does the negatively charged

* As usual, a group derived from acetylene is exceptional.

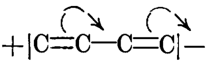
carbon atom. The latter is intensely reactive and easily forms new co-valencies (compare *J. Soc. Chem. Ind.*, *loc. cit.*, for the details of the mechanism of diazo-coupling on this hypothesis). This type of activation involves the displacement of electrons in a particular direction, *e.g.*, from left to right in the figures. Furthermore, since the oxygen acquires a smaller negative charge or an actual positive charge, the process must be the more facile the more highly negatively charged is the oxygen atom before the activation. This explains the descending order of reactivity in the series :



and in the series :

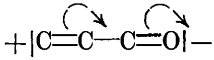


In the acetoxy- and acetylamino-groups, conjugation gives the atom attached to the nucleus a positive charge (compare Rây and Robinson, J., 1925, **127**, 1618). It remains to add that the aromatic nucleus has a special stability of its own which Armit and Robinson (J., 1925, **127**, 1604) consider to be due to the possession of a stable electronic structure, the aromatic sextet. Electronic displacements are resisted by the sextet and it is a fact that the activation of a benzenoid centre in conjunction with any external group is feeble compared with that of an ethenoid complex in similar circumstances. Thus nuclear alkylation by the action of an alkyl halide on a crotenoid base occurs only with the more active aromatic systems. In the course of this investigation our views on the part played by the phenomenon of conjugation in organic chemistry have been more clearly focussed and it now appears possible to classify conjugated systems without arbitrary assumptions. Among the unit reactive groupings from which more complex structures may be derived, especial interest attaches to the highly unsaturated centres * typified by C=C, C=O (C≡N, N=O, etc.), and -O- (-NR-). Of these, C=O alone is kationoid. Certain groupings, C—R, to which definite conditions are attached, must be included. Combining the unsaturated groups two at a time in every possible way, we get :

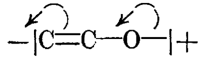
(1) C=C—C=C; *butadienoid*; polarisation—  $+|C{=}C{-}C{=}C|-$; reactivity—anionoid.

Examples are isoprene, aromatic hydrocarbons.

* Certain special structures (ketens, acetylenes) are not considered and it is not suggested that the classification is a complete one.

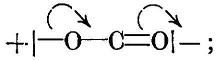
(2) $C{=}C{-}C{=}O$; *crotonoid*; polarisation—  $+|C{=}C{-}C{=}O|-$; reactivity—kationoid.

Examples are methylenemalonic ester, mesityl oxide.

(3) $C{=}C{-}O{-}$; *crotenoid*; polarisation—  $-|C{=}C{-}O{-}|+$; reactivity—anionoid.

Examples are ethyl β-aminocrotonate, dimethylaniline, resorcinol.

(4) $-O{-}C{=}O$; neutralised system; polarisation—

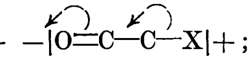

$$+|{-}O{-}C{=}O|-;$$

reactivity—feebly kationoid at C and special characters (see below).

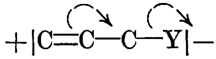
Examples are esters, amides, dianisylideneacetone.

(5) $O{=}C{-}C{=}O$, *quinonoid*, and (6) $-O{-}O{-}$, *peroxidic*, are heterogeneous systems which we do not propose to discuss.

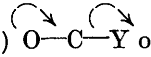
Many more complex combinations of the unsaturated units are possible and especially it will be recognised that all the systems may be expanded by the inclusion of further $C{=}C$ groups. In addition there are derived forms of which the following are the most important.

(7) $O{=}C{-}C{-}X$, where X is an atom or group independently capable of separating with a positive charge; *semi-crotonoid*; polarisation—  $-|O{=}C{-}C{-}X|+$; reactivity—dissociation; often followed by rearrangement of the negative ion and anionoid character exhibited by the carbon atom previously joined to X. The process is analogous to the dissociation of a carboxylic acid.

Examples are acetone, 2 : 4-dinitrotoluene, ethyl α-bromoacetoacetate.

(8) $C{=}C{-}C{-}Y$, where Y is an atom or group independently capable of separating with a negative charge; *allyloid*; polarisation—  $+|C{=}C{-}C{-}Y|-$; reactivity—kationoid.

Examples are phenyl allyl ether (Claisen and Tietze, *Ber.*, 1925, **58**, 275), geraniol.

(9)  $O{-}C{-}Y$ occurs in $MeO{\cdot}CH_2Cl$, etc.

The General Polar Effect.—Conjugation occurs by virtue of electronic displacements which produce an alternating polar effect * as

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* An alternating polar effect in a chain $\overset{-}{A}\overset{+}{B}\overset{-}{C}\overset{+}{D}\overset{-}{E}$ does not mean and never has meant either to Lapworth or to Robinson that the atoms are alternately positively and negatively charged. The phrase is taken to imply that evidence exists that in certain reactions, due to separate polarisations, A, C, or E may exhibit anionoid character and, on the other hand, one of the centres B or D may exhibit kationoid character. The alternation of

an inevitable consequence of the laws of valency operating in relation to changes in co-valency. Electronic displacements which do not involve co-valency changes require no alternation and may be continuous but diminishing in degree along a chain (compare Lapworth and Robinson, *Nature*, 1923, **112**, 722). Such displacements should occur in almost all types of molecules and will be propagated by electrostatic induction (Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; "Valence and Structure of Atoms and Molecules," pp. 84, 143; Thomson, *Phil. Mag.*, 1923, **46**, 497; Lowry, *Trans. Faraday Soc.*, 1923, **18**, 293; Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, **46**, 2475). We concur * with Lucas and Moyse (*ibid.*, 1925, **47**, 1459), for instance, in their application of the theory to the case of the addition of hydrogen bromide to Δ^2-pentene. The general effect of charged centres is obvious and Thomson (*loc. cit.*) has suggested both practical and theoretical methods of estimating the disposition of electrostatic doublets in various types of atomic combinations. In addition, the general effect of a group R can often be estimated by a consideration of the strength of the acid $R{\cdot}CO_2H$. All the evidence goes to show that hydrogen has a greater attraction for electrons than has the methyl group; we shall find it more convenient to express this statement in the converse form. This effect is represented, as in former cases (Malkin and Robinson, J., 1925, **127**, 370), by a straight arrow showing the direction in which the electrons are displaced. As an example of the interaction of the two types of electron displacement, we consider the carboxylic acids $R{\cdot}CO_2H$. The polarisation $O\overset{\curvearrowleft}{\underset{(b)}{=}}C\overset{\curvearrowleft}{\underset{(a)}{-}}OH$ proceeds until the positive charge † on the hydroxyl oxygen increases to such an extent that the proton is weakly held and can be removed by solvent molecules. The two oxygen atoms then divide the negative charge and assume identical functions. The displacement (*a*) is clearly the more fundamental process, but (*b*) is, however, a necessary

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stable and less stable octets was suggested by Kermack and Robinson (*loc. cit.*) as a possible, admittedly speculative, explanation of the tendency underlying the exhibition of this property. This suggestion was never intended to be regarded as a *mechanism* of activation, for which Kermack and Robinson retained an electronic translation of the theory of partial dissociation of conjugated complexes as developed by Robinson and Robinson (*loc. cit.*).

* Except, naturally, in considering that clear cases of the operation of continuous electron displacement dispose of the necessity for recognising the other type of displacement which occurs in conjugated systems.

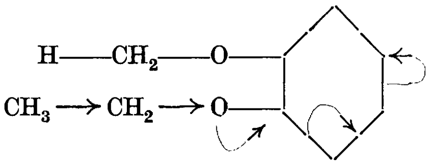
† Positive and negative are taken to mean also less negative and less positive respectively. Similarly, a smaller attraction is relatively a repulsion, and *vice versa*.

accessory in providing a means of adjustment of the disturbed co-valency of the carbon atom.

Contrasting $\mathrm{R}\longrightarrow\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{OH}}$ and $\mathrm{R'}\longleftarrow\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{OH}}$ it is apparent that the group R in repelling electrons *competes* with OH and to some extent inhibits the process (*a*), whilst the opposite is true of a group R′ which attracts electrons. Thus R′·CO_2H is a stronger acid than R·CO_2H. The case of the phenols is simpler and again R′·OH should be a stronger acid than R·OH. Conjugation $\begin{matrix}\mathrm{R}\!-\!\!-\!\!-\!\mathrm{C}{=}\mathrm{O}\\ \curvearrowright\ \ \ \mathrm{OH}\end{matrix}$ is also a factor, weakening an acid. This system does not exclude the consideration of the effect of a steric factor * (Flürscheim, J., 1909, **95**, 718) and is in excellent agreement with the available data.

The whole of the foregoing can be independently justified and we proceed to consider how these principles apply to the results recorded in the preceding communications.

In the ethyl ether of guaiacol we have the condition



because the methyl group exercises a greater repulsion on electrons than hydrogen does. Therefore the polarisation of the crotenoid system, including the oxygen of the ethoxyl group, is facilitated as compared with the other system, not represented, which includes the oxygen of the methoxyl group. It follows that ethoxyl should have a higher directive power than methoxyl † (Found : EtO, 135; MeO, 100). The substitution of methyl for a second hydrogen atom should still further increase the directive power (Found : $Pr^{\beta}O$, 150). It is very interesting, however, that in the catechol series EtO, among *n*-alkyloxy-groups, appears to reach a maximum directive power (Found : EtO, 135; $Pr^{\alpha}O$, 128; *n*-C_4H_9·O, 123). This phenomenon we regard as due to the fact that as the chain lengthens a greater proportion of the general effect is distributed over the molecule and a smaller proportion, therefore, is effective through the attached atoms of the chain. Thus the ratio Directive

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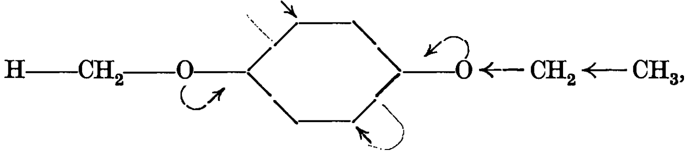
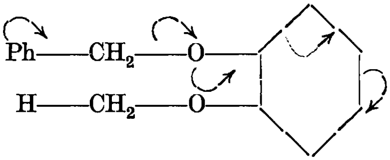
* Possibly also an electrical effect exercised across the intervening space rather than through the chain.

† The case of OH itself as against OMe cannot be considered on similar lines on account of the possibility of ionisation or removal of the proton from OH by the reagent.

power RO/Directive power MeO can be expressed as $y + a/x + a$,* where R is a higher alkyl group, y is its directive power apart from a; x is the directive power of methoxyl apart from a, a is a quantity depending on the general polar effect of the excess methylene groups in R — Me and is that portion of the effect which, owing to its distribution over the molecule, goes to assist the polarisation of the crotenoid system, including the oxygen of the methoxyl groups. As a increases, the ratio will approach some minimum value greater than 1. Our results can be interpreted on the assumption that the terminal methyl group of a *n*-propyl group exercises a general effect which is largely distributed over the molecule and only to a small extent transmitted through the attached chain. In the series of catechol experiments it is important to observe that the general effect must assist both conjugations, and the interest of parallel experiments in the quinol series is that this is no longer true. Thus in *p*-ethoxyanisole,



it is clear that the conjugations of the crotenoid systems themselves involve electronic displacements in opposing directions. The argument used in the catechol series still holds; ethoxyl should have a greater directive power than methoxyl, but if a portion of the general effect of the additional CH_2 of the ethoxyl is distributed, we can write: Directive power of EtO/Directive power of MeO = $y' + a'/x' - a'$. It might accordingly be anticipated that ethoxyl would have a higher relative directive power in the quinol than in the catechol series (Found: EtO in catechol series, 135; EtO in quinol series, 163). Furthermore, as a' increases, the value of the ratio $(y' + a')/(x' - a')$ must also increase, and the theory, which predicts a lower value for $\mathrm{Pr}^{\alpha}\mathrm{O}$ as compared with EtO in the catechol series, also requires in the quinol series that $\mathrm{Pr}^{\alpha}\mathrm{O}$ should be greater than EtO (Found: $\mathrm{Pr}^{\alpha}\mathrm{O}$ in quinol series, 180). In the benzyl ether of guaiacol we encounter one of the postulated conjugated systems (allyloid):



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* The form of this expression is justified if x, y, a are taken as representing the number of occasions in unit time on which the different factors concerned lead to effectual polarisations.

In such a case the whole chain is not to be regarded as *one* conjugated system. The allyloid system * tends to assist the oxygen atom to acquire a negative charge, and this assists the related crotenoid system to function † (Found : $CH_2Ph\cdot O$, 113; MeO, 100).

In the *m*-methoxybenzyl group (directive power, 92), the methoxyl group has the general effect anticipated on the basis of Thomson's deductions concerning the situation of electrostatic doublets, and the whole group exercises less repulsion on electrons than the methyl group does. This is far more pronounced with *m*- and *p*-nitrobenzyloxy-groups (directive powers, 67). The identity of the directive powers of these two groups was unexpected and led us to adjust our views on conjugation in the direction now indicated. It must not, however, be hastily concluded that the nitro-group produces no alternating effect, even in these experiments, since the fact that *p*-nitrobenzoic acid is slightly stronger than the *m*-isomeride indicates a weak alternate effect. In the *m*-nitrobenzyloxy-group, we might have a slightly stronger general effect and a weaker alternating effect (crotonoid-type) than in the *p*-nitrobenzyloxy-group, and these small variations may balance. However this may be, the results show that if the nitro-group does produce an alternating effect it must be a very small one and this is normal because the reaction examined is one in which the substance exhibits anionoid character and conjugation of nitroxyl with the aromatic nucleus leads to the exhibition of kationoid properties. In the catechol series, for a group like the *p*-nitrobenzyloxy-group we have : Directive power of group/Directive power of MeO = $(z - b)/(x - b)$ and in the quinol series the ratio becomes $(z' - b')/(x' + b')$. Thus in the quinol series such a group should have a smaller relative directive power than in the catechol series (Found for the *p*-nitrobenzyloxy-group : in the catechol series, 67; in the quinol series, 38). In connexion with these deductions, it is important to notice that there

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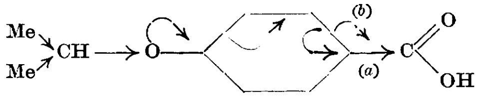
* It should be noted that the distribution of affinity in the butadienoid, crotenoid and allyloid systems on our electronic basis coincides with the requirements of Flürscheim's theory, but this is not the case in the crotonoid and semi-crotonoid types.

† The occurrence in some substances of quite complex combinations of general and alternate effects can be foreseen. Thus *p*-*iso*propoxybenzoic acid should be weaker than anisic acid or even than *p*-*n*-propoxybenzoic acid :



Here we have a general effect reinforcing a crotenoid system the polarisation of which produces a general effect (*a*), *or* a conjugation effect (*b*), or both; thereupon influencing the carboxyl as explained above.

are no side reactions to complicate the issue and that in all cases we have measured the whole effective directive power of the groups concerned. Consequently the small differences between x and x', y and y', and z and z' are not likely to affect the validity of our conclusions. We do not claim that the interpretation is more than an approximation to the truth.

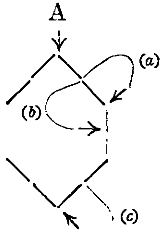
The point of view now adopted is one from which the general problem of orientation in aromatic substitution can be surveyed and we regard it as necessary to approach the subject in the following stages, which are of diminishing importance.

(1) Consideration of the circumstances of the reaction and especially whether the reagent is anionoid or kationoid.

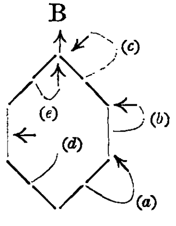
(2) Consideration of the conjugated systems.

(3) Consideration of the general effect of attached groups on the conjugated systems.

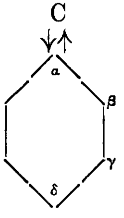
We will confine ourselves to the cases such that there is no attached group conjugated with the nucleus and the reagent is kationoid (Br_2, HNO_3, etc.). In other words, we contemplate a normal benzenoid (butadienoid) system exhibiting anionoid character and wish to deduce from fundamental principles the nature of the effect of attached groups. In the case of a group, A, which repels electrons more than hydrogen does we have the arrangement (I). Here the crowding of electrons round C_α will facilitate, by repelling $C_\alpha C_\beta$ co-valency electrons, the polarisation of that particular butadienoid system which starts with C_α. The electron will be captured by C_β (process *a*; *o*-substitution) or, if not, a $C_\alpha C_\beta$ co-valency electron will become a $C_\beta C_\gamma$ co-valency electron (process *b*). C_γ, to recover its normal co-valency, must then correspondingly relinquish an electron to C_δ (process *c*; *p*-substitution). An alternative statement is that the ring carbon atom around which the density of electrons is greatest most easily becomes the positive end of a conjugated polarised complex. The applications will be obvious—toluene and *tert.*-butylbenzene are in the same category. In the case of a group B, which has a *strong*



Case I.



Case II.



Case III.

attraction for electrons (II), it is easy to see in a general way that the circumstances are reversed, but in order to make the argument clear we take an extreme instance such that B has a definite positive charge. The electrical field emanating from B then produces positive electrification in diminishing degree over the portion of the molecule represented. One consequence is that all displacements of electrons in activation will tend to be towards B, and this inhibits para-substitution. Of all the remaining possible displacements (*a*, *b*, *c*, *d*, *e*), that indicated by (*a*) is the most likely to lead to reaction, because reaction depends on the acquirement of a negative charge and of all the carbon atoms which can be activated C_γ has the smallest positive charge. A less degree of electron displacement, therefore, will activate C_γ than will suffice for C_β. In order of preference we find in this case *m*-substitution, *o*-substitution, *p*-substitution, whilst displacement of the group B is also possible. An alternative statement is that the carbon atom (C_δ) furthest removed from the positive charge is least positive or most negative and most easily acquires a more positive charge and therefore most readily functions as the positively charged end of a polarised ethenoid or butadienoid complex. We cannot lay down any rules in regard to the required strength of the positive charge on B. The nitrogen of the nitro-group is positively charged if we accept the formulation $=\overset{|}{O}-\overset{|}{N}=\overset{|}{O}-$ in which each line represents an electron pair and it would appear that this group is effective even when separated from the nucleus by one carbon atom (Holleman, *Rec. trav. chim.*, 1895, **14**, 121).

Substitution in the *m*-position might also occur in a benzylammonium ion.

The carbon atoms of the carboxyl, carbonyl and trichloromethyl groups can also be regarded as positively charged on the basis of independent evidence. This theory seems to harmonise better than any other which has been advanced with the facts of substitution in polycyclic aromatic groups, but a separate discussion of this subject is necessary. In the case of a group C (III) which in some phases attracts and in others repels electrons we anticipate predominating *o*-*p*-substitution because the phase in which electrons are repelled provides a favourable opportunity for activation leading to anionoid character, whereas the other phase in no way contributes to activation and in fact inhibits it.

In the case (I) a negative charge is distributed over the nucleus and anionoid character is intensified, leading to ready reaction, whilst in case (II) the distributed positive charge inhibits the exhibition of anionoid character. We can in fact estimate the approximation of a group X to the types A or B by observing the ease of substitution of X–Ph as compared with that of benzene.

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[*Received, June* 18*th,* 1925.]