CXXI.—*Mobile-anion Tautomerism. Part I. A Preliminary Study of the Conditions of Activation of the Three-carbon System, and a Discussion of the Results in Relation to the Modes of Addition to Conjugated Systems.*

By HAROLD BURTON and CHRISTOPHER KELK INGOLD.

ONE of the advantages which accrue from the interpretation of the reactions of Organic Chemistry in the light of the electronic theory of valency is that similar laws are seen to govern apparently diverse types of phenomena, such as mobility and equilibrium in tautomeric systems and orientation in aromatic substitution. Thus in the field of prototropic change, the dependence of mobility on the ionising properties of the system as exhibited by the stability of its sodium and potassium salts was already recognised (Ingold and Piggott, J., 1922, 2381); but the application of the electronic theory showed also that groups which contribute to the stability of the electromeric anion act as they do owing to their affinity for the negative charge, which circumstance renders the same groups strongly *m*-orienting in aromatic substitution: a correct interpretation of the mechanism of the two phenomena renders the agreement complete (Ingold, Shoppee, and Thorpe, J., 1926, 1477; Cooper and Ingold, J., 1927, 836).

It can be seen in a general way that opposite conditions will prevail in mobile-anion tautomerism (anionotropy), and that a somewhat similar parallelism should subsist between the power of groups to confer mobility and their *op*-directing efficiency in aromatic substitution; thus may the greater stability of the ionised salts of nitrogen- than of oxygen-pseudo-bases be correlated with the greater *op*-directing power of ·NRR′ than of ·OR. At the same time, certain differences would be expected, so that it would be false to invert mechanically all conclusions relating to the previous comparison. As to this point, an example will make our meaning clear.

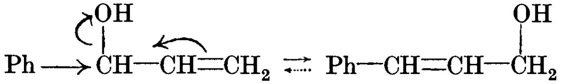
The conferment of prototropic mobility by the groups $\cdot SO_2R$ and ·NR′R″R‴ is at present being studied in these laboratories and the complete results are not yet available, but on theoretical grounds it is not to be expected that these groups, despite their great *m*-orienting power, would confer a correspondingly greater degree of mobility on an attached three-carbon system than ·COMe, for example; for although the groups $\cdot NR_3$, etc., must attract electrons very strongly, they cannot provide a seat for the anionic charge without expanding an already-filled, stable electron group, or commencing a new group; they might, however, act indirectly by increasing the toleration of an adjacent carbon atom for a lone-pair. Thus in the conferment of prototropic mobility, $\cdot NR_3$ and COR necessarily act by different mechanisms, whereas in *m*-orientation they act, mainly at any rate, by an identical mechanism (Ingold and Shaw's "Case 2," J., 1927, 2918; compare Cooper and Ingold, *loc. cit.*; Baker, Cooper, and Ingold, this vol., p. 429); therefore we cannot equate their effects in the two cases. Now in the realm of anionotropy there is a corresponding difference between the functions of the activating groups $\cdot CH_3$ and $\cdot OR$: the former may repel electrons (as compared with $\cdot H$) and so increase the toleration of an adjacent carbon atom for a shared sextet, but it cannot without disruption provide a seat for the cationic charge; the latter group, on the other hand, can readily do so by sharing one of its lone-pairs. A precisely similar difference of mechanism relates to the *op*-orienting behaviour of these groups in aromatic substitution (Ingold and Shaw's "Cases 1" and "3"). Thus the connexion between anionotropy and *op*-orientation should be of a simpler and more direct kind than the previously studied connexion between prototropy and *m*-orientation.

These considerations led us to embark upon a general investigation on the effect of groups in promoting anionotropic change, and in this paper some preliminary results are given for the systems

$$Ar{\cdot}CHX{\cdot}CH{:}CH_2 \rightleftharpoons Ar{\cdot}CH{:}CH{\cdot}CH_2X$$
$$Ar{\cdot}CHX{\cdot}CH{:}CHAr' \rightleftharpoons Ar{\cdot}CH{:}CH{\cdot}CHX{\cdot}Ar'$$

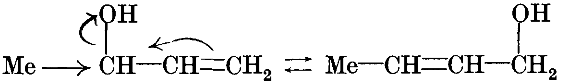
where the potentially mobile anion, X, is OR or Hal. Gillet appears to have been the first (*Bull. Soc. chim. Belg.*, 1922, **31**, 366) to direct attention to the significance of polar factors in three-carbon anionotropy, and to have suggested what is undoubtedly a correct partial explanation of 1 : 4-addition of halogens, namely, that 1 : 2-addition is succeeded by anionotropic change (compare Prévost, *Compt. rend.*, 1927, **184**, 1460; Farmer, Laroia, Switz, and Thorpe, J., 1927, 2937; Farmer, Lawrence, and Thorpe, this vol., p. 729). Gillet formulates his conclusions as follows: "If in the system $\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}(X)$ the radicals at C_3 are as a whole more negative than those at C_1, the most negative radical (X) attached to C_3 will tend to migrate to C_1." This view at once led its author into difficulties, however, for in the majority of available examples an alkyl group attached to C_3 appeared to be the predominating factor determining the departure of X. Thus Gillet was forced to draw a distinction between "migrations vraies" (those which followed his rule), and "transpositions hydrolytiques" (those which did not). The latter were regarded as dependent on the preliminary addition of water or some other addendum to the double bond and subsequent fission in another direction—despite the fact that there is no clear distinction between the conditions of occurrence of the change in two series of cases, and that these conditions are frequently such as to render the addition-and-elimination theory extremely improbable. Reference may also be made to a recent paper by Prévost (*Compt. rend.*, 1927, **185**, 132), who, following up Lowry's explanation of prototropy (*Deuxième Conseil de Chimie, Congrès Solvay*, 1925, p. 156), applies to anionotropy the theory of alternate polarities in the extreme form in which the carbon double bond is regarded as semi-polar; this conception, however, does not enable Prévost to advance the problem of elucidating the structural conditions under which anionotropy is manifested.

In the system :

(I.)  (II.)

$$\mathrm{Ph}\longrightarrow\overset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH}=\mathrm{CH_2}\rightleftharpoons\mathrm{Ph}-\mathrm{CH}=\mathrm{CH}-\overset{\mathrm{OH}}{\mathrm{CH_2}}$$

the degree of mobility is not very great, for the two alcohols can be obtained as separate individuals and we have prepared from each a crystalline *p*-nitrobenzoyl derivative. It is true that Valeur and Luce (*Bull. Soc. chim.*, 1920, **27**, 611) claim to have transformed (I) into (II) by means of dilute sulphuric acid, but we have not succeeded in repeating this observation, and, without controverting it, may state that our numerous attempts have given us the impression that it would be very difficult to effect a *smooth* conversion in the manner indicated. On the other hand, we find that the alcohol (I) is smoothly and completely converted into the acetate of (II) by boiling with acetic anhydride. Furthermore, Moureu and Gallacher (*ibid.*, 1921, **29**, 1059) obtained from the two alcohols the same crystalline bromide, which, they surmised, was cinnamyl bromide; and we have proved the correctness of this structure by ozonolysis, whereby benzoic acid and bromoacetaldehyde were obtained. The *p*-tolyl analogues of (I) and (II) can also exist separately, but the former is converted by acetic anhydride into the acetate of the latter easily and completely with no indication of perceptible reversibility. The reaction is more facile than in the phenyl series. Smooth conversion into substituted cinnamyl bromides occurs when the *p*-tolyl analogues of (I) are treated with cold hydrogen bromide in acetic acid solution. It would, of course, be expected that the tendency to migration of different potentially mobile anions (X) contained in systems otherwise identical would follow the order of anionic stability (strengths of the acids HX), as, for example, OH < OAc < Br. Further it follows from the presumed influence (represented by ⟶ in I) of the aryl group in increasing the toleration of C_α for the shared sextet left on separation of $\overset{\ominus}{OH}$, that the equilibrium in systems such as $I \rightleftharpoons II$ should strongly favour form II, the more so the stronger the activation by Ar—and this is undoubtedly the case. On the other hand, there is evidence that in systems of the form

(III.)  (IV.)

$$Me \longrightarrow \overset{\curvearrowleft OH}{\overset{|}{CH}}—CH{=}CH_2 \rightleftarrows Me—CH{=}CH—\overset{OH}{\overset{|}{CH_2}}$$

not only is the mobility less, but also there is a less uneven relation between the forms at equilibrium. Thus Baudrengheim found (*Bull. Soc. chim. Belg.*, 1922, **31**, 160) that each alcohol yielded its own acetyl derivative on boiling with acetic anhydride, although a slight interconversion in the sense III ⟶ IV was observed when a mixture of acetic anhydride and sulphuric acid was used. Furthermore, both alcohols yielded an equilibrium mixture of isomeric chlorides, in which, although the chloride of (IV) was certainly the main constituent, the chloride of (III) was present in sufficient amount to enable it to be separated by distillation. Both these comparisons with the phenyl case are consistent with the view that the phenyl group with its looser electronic system can more completely neutralise the positive charge left on C_α by the separation of the anion than can the methyl group. Comparison with the effect of phenyl in promoting the formation of styrene from β-phenylethylammonium salts (Hanhart and Ingold, J., 1927, 997) establishes yet another point. In this reaction the phenyl neutralises the negative charge left on carbon by the separation of a cation (hydrogen). It follows that in both cases the *primary* change is the ionisation ($\overset{\curvearrowright}{—OH}$, above), and that the action of the facilitating group (⟶ above) is a compensating, not an initiating, process.*

For the investigation of the αγ-diarylated systems we have employed two methods of diagnosis, one of which, namely, ozonolysis, needs no explanation. The other depends on the prototropic change exemplified by

$$C_6H_5{\cdot}CH(OH){\cdot}CH{:}CH_2 \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_3$$

(Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209) and

$$C_6H_5{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$$

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* The power of the phenyl group (which is enhanced in *p*-diphenylyl and other polynuclear groups) to compensate electrostatic disturbances of either sign in an attached atom is doubtless the cause of the dissociability of the hexa-arylethanes and allied compounds.

(Nomura, *ibid.*, 1925, **37**, 1245). These reactions take place quantitatively in the presence of alcoholic alkali,* and the ketones formed can readily be synthesised by adaptations of the acetoacetic ester method, and thus identified. The first of the examples cited above shows that hydroxyl-migration does not precede the prototropic change, and confirmation of this is to be found in experiments described below; nor would a preliminary change of this kind be expected, since the catalyst (alkali) is essentially one for promoting *cationotropic* change (Ingold, Shoppee, and Thorpe, *loc. cit.*).

Our principal object in this part of the investigation was to obtain a comparison of the activating effects of the groups $p\text{-}CH_3{\cdot}C_6H_4{-}$ and $p\text{-}Cl{\cdot}C_6H_4{-}$, since only the latter contains unshared electrons by the sharing of which a seat can be provided for the positive charge on the electromeric cation. No difficulty was experienced in preparing (by the usual Grignard method) the member (V) of the system

$$\text{(V.)}\quad (p)\ Me{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C_6H_5 \rightleftharpoons (p)\ Me{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C_6H_5\quad \text{(VI.)}$$

It was crystalline, and showed no tendency to pass into its isomeride (VI). Re-arrangement with alcoholic alkali yielded exclusively the crystalline ketone $(p)\ Me{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, which was synthesised *via* ethyl α-benzyl-*p*-toluoylacetate. On the other hand, the acetate prepared from (V) with acetic anhydride was manifestly an equilibrium mixture : with alkalis it yielded a mixture of the ketones $C_7H_7{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$ and $C_7H_7{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$ (both synthesised) probably containing an excess of the latter, although our separation was not sufficiently complete to enable us to assert this definitely; furthermore, ozonolysis of the acetates, followed by hydrolysis of the ozonides, yielded considerable quantities of *p*-tolualdehyde, *p*-toluic acid, and mandelic acid, and smaller quantities of benzoic acid and a very soluble acid which was probably *p*-methylmandelic acid because on further oxidation it gave *p*-toluic acid. That the equilibrium is probably in favour of the acetate of (VI) is, of course, consistent with the anticipated greater effect of $CH_3\rightarrow C_6H_4\rightarrow C^{\alpha}$ than of $H{-}C_6H_4\rightarrow C^{\alpha}$ in compensating for the loosening of the anion from its attachment to C_{α}. On the other hand, in the *p*-chloro-series, not only the acetates,

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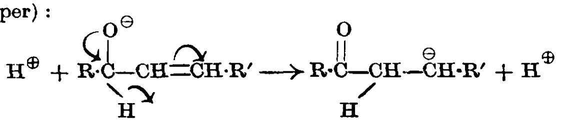
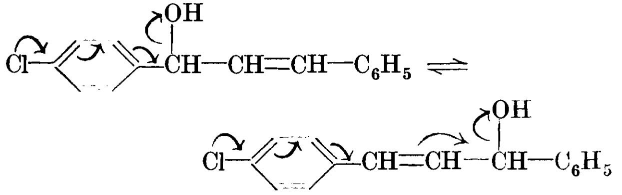
* They probably take place through the anion by the " pinacolic " electron-displacement (see Ingold and Shoppee, this vol., p. 365; Shoppee, forthcoming paper) :



but also the alcohols themselves, passed into an equilibrium mixture, so that we were unable to obtain the individuals (VII) and (VIII) separately :

(VII.)

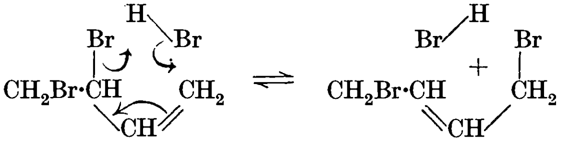


(VIII.)

In this case, the indications were clearly that (VIII) is the main isomeride. Treatment with alkali yielded a large proportion of p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5}$ and a small amount of p-$\mathrm{Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5}$ (both synthesised), and hydrolysis of the mixed ozonides gave p-chlorobenzoic and mandelic acids in large quantity, together with a little benzoic acid, and a very soluble acid presumed to be p-chloromandelic acid from its oxidation to p-chlorobenzoic acid.

Thus the order of facilitation of three-carbon anionotropy by α-substituents is $p\text{-}\mathrm{Cl{\cdot}C_6H_4{\cdot}} \gg p\text{-}\mathrm{Me{\cdot}C_6H_4{\cdot}} > \mathrm{C_6H_5{\cdot}} \gg \mathrm{CH_3{\cdot}} > \mathrm{H}$; which agrees, as it theoretically should, with the *op*-orienting sequence $\mathrm{Cl} > \mathrm{Me} > \mathrm{H}$ as inferred in the ordinary way from the proportions of isomerides formed in benzene substitutions.

As regards the function of catalysts, these must obviously be of such a kind that they have a sufficient affinity for the mobile group. Acids (*e.g.*, HBr, H_2SO_4) might act in this way (either directly or *via* the hydronium ion), as also might polarised or readily polarisable organic compounds such as acid anhydrides (*e.g.*, Ac_2O). As to the precise history of the eliminated anion, we are prepared at present to entertain two views; either (as is assumed above) it may leave the molecule completely in covalent or molecular combination with the catalyst, to be subsequently returned to another molecule in one of the two possible positions of reunion; or, in certain cases, concomitantly with the elimination (ionisation) of the group, its equivalent may be introduced into the new position by an internal cyclic process such as



We hope at a later date to be able to submit further evidence on this question.

Addition to Conjugated Systems.

Although Thiele's writings leave little room for doubt that he originally intended his hypothesis to imply universal 1 : 4-addition in conjugated systems of two double linkings, it has long been known that this position cannot be maintained, so that the Thiele hypothesis, even with its later extensions, has not the diagnostic value which it was once imagined to possess. In short, there exists no theory of orientation in additions to conjugated unsaturated systems comparable in range and definition with the orientation theory which has been developed for substitutions in aromatic systems. Chandrasena and Ingold (J., 1922, **121**, 1306) formulated certain rules for conjugative additions, but these rules were avowedly empirical, and it is our view that they require supersession. The provision of data for the development of this subject on more fundamental lines has been one of the major objects of the investigation outlined above.

The subject divides itself into three main parts according to the nature of the addendum, and then into sub-sections depending on the structure of the unsaturated complex. The general scheme of classification * may be indicated as follows :—

Case 1. Both parts of addendum stable as anions (Cl_2, Br_2, ICl, OHCl, etc.). Structural influences (*a*) favour, (*b*) inhibit, anionotropic mobility.

Case 2. One part of addendum stable as anion, and the other as cation [HBr, HCl, HCN, $NH_2{\cdot}OH$, $CH_3{\cdot}NO_2$, $CH_2(CO_2Et)_2$, etc.]. Structural influences (*a*) favour, (*b*) inhibit, anionotropic mobility.

Case 3. Both parts of addendum stable as cations (H_2).

In this paper it is proposed to deal only with Cases 1*a* and 2*a*, because it is to these that the new experimental material primarily relates. Our general theoretical method will be fairly obvious from the examples taken, but we prefer to postpone actual discussion of the remaining four divisions of the subject until the experimental work appropriate to them has been completed.†

Case 1*a*. *Example : Addition of Bromine to Conjugated Unsaturated Hydrocarbons.*—In any given instance two questions arise,

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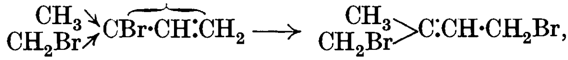
* This must be interpreted with due care, and two possible pitfalls may be indicated. (1) If a group retards one kind of tautomeric change, it seems safe to assume that it will promote the other; but the converse does not necessarily hold, as is indicated by the example on p. 907. (2) Although a group will normally exhibit greater stability as one kind of ion, special structural conditions may reverse its rôle; thus we hold that bromine is a potential cation in $CH_3{\cdot}CO{\cdot}CHBr{\cdot}CO_2Et \longrightarrow CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, though we are aware that contrary views have been expressed.

† For partial statement of application to Case 3 see *Chem. and Ind.*, 1928, **47**, 269.

one of which is more remote than the other. The less remote, and practically more important, question is : What is the *stable* product ? For in the case under consideration, only potentially mobile anions are introduced by the addendum, and the groups already present favour anionotropic change ; it follows that unless special experimental precautions are taken the stable product will be the one isolated. A theoretically interesting, but much more difficult question is : What is the *initial* product ? This will be considered afterwards.

The stable product. To discover this by the method to be given, the simplest plan is to make an assumption as to the structure of the initial product. We shall suppose that a 1 : 2-dibromide is first formed. The accuracy of this assumption will be considered later, when it will also appear that it is not important for the purpose in view that it should be accurate.

Butadiene. Let it be assumed that $\mathrm{CH_2Br{\cdot}\overbrace{CHBr{\cdot}CH{:}CH_2}}$ is first formed. The bracket indicates the anionotropic system, and the activating group is $\cdot\mathrm{CH_2Br}$, which, by analogy with $\cdot\mathrm{CH_2Cl}$, must be a very weak *op*-orienting group—weaker than $\cdot\mathrm{CH_3}$ and therefore not incomparable with ·H. Anionotropic change to the 1 : 4-product will therefore (compare activation by $\mathrm{CH_3}$, p. 907) be notably incomplete and we should expect a substantial amount of 1 : 2-by-product to accompany the 1 : 4-main product. [Farmer, Lawrence, and Thorpe find 1 : 2-dibromide 30%, 1 : 4-dibromide 70% on bromination with bromine in acetic acid at 4° (*loc. cit.*).]

Isoprene. Here an additional methyl group is present to promote the change  $\left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Br}\end{matrix}\right\rangle\overbrace{\mathrm{CBr{\cdot}CH{:}CH_2}} \longrightarrow \left.\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2Br}\end{matrix}\right\rangle\mathrm{C{:}CH{\cdot}CH_2Br}$, so that the proportion of 1 : 4-dibromide should be somewhat higher than in butadiene [Staudinger, Muntwyler, and Kupfer find that isoprene dibromide, which is a liquid, consists mainly of the 1 : 4-compound, but the precise proportion is not known (*Helv. Chim. Acta*, 1922, **5**, 756).] (*A*).

βγ-Dimethylbutadiene. For similar reasons, the proportion of 1 : 4-compound should be higher than in butadiene. [The recorded data (Kondakow, *J. pr. Chem.*, 1900, **62**, 171) do not appear to be inconsistent with this inference, despite the interpretation given in Beilstein's " Organische Chemie " (4$^{\text{te}}$ Aufl., I, 218) in which the dibromide is assigned a 1 : 2-formula.]

αδ-Diphenylbutadiene. If $\mathrm{Ph{\cdot}CHBr{\cdot}\overbrace{CHBr{\cdot}CH{:}CH}{\cdot}Ph}$ were first formed, the relatively slow and incomplete change (promoted by $\mathrm{Ph{\cdot}CHBr\cdot}$) to the isomeride $\mathrm{Ph{\cdot}CHBr{\cdot}\overbrace{CH{:}CH{\cdot}CHBr}{\cdot}Ph}$ would be immediately succeeded by the much more rapid and complete change (promoted by Ph·) to Ph·CH:CH·CHBr·CHBr·Ph (compare anionotropic changes promoted by Ph; p. 906). Hence the main product should be the 1 : 2-(= 3 : 4-)dibromide. [This has been established by Strauss (*Ber.*, 1909, **42**, 2867).] (*B*).

α-Phenylbutadiene. Similar considerations show that the main product should be Ph·CH:CH·CHBr·CH_2Br. [Strauss has demonstrated this also (*loc. cit.*, p. 2871).]

Hexatriene. Since vinyl is expected to act like phenyl, the 3 : 4- and 1 : 4-dibromides will not be obtained as stable products, since the former would be comparatively slowly and reversibly transformed into the latter, whilst this would pass rapidly and substantially completely, either into the 1 : 2-isomeride (change facilitated by ·CH:CH_2), or into the 1 : 6-compound (change facilitated by ·CH:CH·CH_2Br). [Farmer, Laroia, Switz, and Thorpe obtained 1 : 2- from *cis*-hexatriene and 1 : 6- from *trans*-, but did not in either case encounter 1 : 4- or 3 : 4- (*loc. cit.*).]

αζ-Diphenylhexatriene. The dibromide should be either 1 : 2- or 3 : 4-, but not 1 : 4- or 1 : 6-. (It has not yet been oriented.)

The initial product. The above provisional hypothesis that 1 : 2-addition precedes the formation of a 1 : 4-dibromide requires consideration. The work of Orton and King (J., 1911, **109**, 1369) and Soper and Smith (J., 1926, 1582) shows that in chlorine-substitution, either by Cl_2 or by HOCl, the molecule, and not either of its ions, is the actual reagent, even in an ionising solvent such as water : it may be assumed that the same is true for halogen addition in all ordinary circumstances. In the light of this conclusion, the experiments of Terry and Eichelberger (*J. Amer. Chem. Soc.*, 1925, **47**, 1067) and of Francis (*ibid.*, p. 2340) are seen to prove that the halogen molecule initially supplies only one halogen atom to the unsaturated substance; thus, to quote one experiment, the second stage of the presumed mechanism

$$CH_2{:}CH_2 + Br_2 \longrightarrow CH_2Br{\cdot}CH_2^{\oplus} + Br^{\ominus} \longrightarrow CH_2Br{\cdot}CH_2Br$$

may be modified by using bromine water containing a soluble nitrate; the nitrate ion then competes with the bromide ion and $CH_2Br{\cdot}CH_2{\cdot}O{\cdot}NO_2$ is formed along with $CH_2Br{\cdot}CH_2Br$. This demonstration applies, however, only to conditions favouring ionisation, and it is not to be expected that under non-ionising conditions a free halide ion would be liberated. Under such conditions the initial product of addition to a conjugated system could only be a 1 : 2-compound, and an elegant demonstration of this has been given by Thorpe and Farmer in the work already quoted. On the other hand, under conditions favourable to ionisation a process analogous to that depicted for ethylene might occur, so that the initial product would more correctly be described as consisting of the ions of the 1 : 2-dibromide. We have, however, already (p. 909) entertained the hypothesis that in an anionotropic change, such as 1 : 2-dibromide ⟶ 1 : 4-dibromide, ionisation (not *necessarily* dissociation) precedes the electromeric transformation, and if the ions are pre-formed, the mechanism is simplified to that extent. Thus the object of this paragraph is to point out that our actual view of the general case, namely,

$$\begin{tikzcd} & & \text{1 : 2-Bromide} & \\ \text{Reagents} \arrow[r] & \text{Ions of 1 : 2-bromide} \arrow[ur, shift left] \arrow[ur, leftarrow, shift right] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] & & \\ & & \text{Ions of 1 : 4-bromide} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & \text{1 : 4-Bromide} \end{tikzcd}$$

remains consistent with the results obtained by the use of the simplified hypothetical mechanism.

Case 2a. Examples: Additions of Hydrogen Bromide and Hydrogen Cyanide to Conjugated Unsaturated Acids and Esters, and Michael's Addition Reaction.—The potentially mobile cation (hydrogen) may be assumed to enter *via* the carbonyl oxygen; its final position will normally be the α-position unless the conditions are suitable for the αβ–βγ-prototropic change (Kon, Linstead). The position of stability of the mobile anion is of more interest in relation to the experimental evidence submitted in this paper. That anionotropic change will control the situation is obvious in the case of hydrogen bromide-addition, and the reversibility of the Michael reaction, and its analogy with hydrogen cyanide-addition appears to guarantee that the same conclusion can be extended to these reactions.

The stable product. A few examples only will be mentioned, and for brevity the reasons for the theoretical conclusions which are given will be replaced by letters referring to some previous paragraph containing an argument sufficiently similar to the one omitted.

Sorbic acid and its esters. Lettering the butadiene chain as usual from the carboxyl group, both αβ- and αδ-addition would be expected, the potential anion being at C_β or C_δ (*A*). [The occurrence of αδ-addition of malonic ester has been established.]

Cinnamylideneacetic and cinnamylidenemalonic acids and their esters. Here *only* αβ-addition, and not αδ-addition, should occur, the anion going to C_β (*B*). [The addition of hydrogen bromide, and of malonic ester, to cinnamylideneacetic acid (or ester), and the addition of hydrogen bromide, hydrogen cyanide, and nitromethane to cinnamylidenemalonic acid (or ester), have been investigated. In all five cases, the products are those of αβ-addition.]

The initial product. The remarks under a corresponding heading relating to bromine-addition apply with a few obvious modifications to hydrogen bromide addition. The additions in alkaline solution of hydrogen cyanide, malonic ester, etc., are, however, in a different category, and the question of the initial product does not seriously arise, since in general it will consist of the anions (formed simultaneously) of the two possible addition-products (Cooper and Ingold, J., 1926, 1868); the attachment of the cation, we assume, occurs subsequently (often during acidification).

Action of Phosphorus Pentachloride on αβ-Unsaturated Ketones and Related Reactions.

This subject is mentioned as another which receives satisfactory explanation on lines similar to those illustrated above. The reaction may be exemplified by $C_6H_5 \cdot CO \cdot CH{:}CH \cdot C_6H_5 \longrightarrow C_6H_5 \cdot CCl{:}CH \cdot CHCl \cdot C_6H_5$, and the interpretation we should apply to the more complicated instances will be obvious to any who compare this paper with Strauss's original memoirs (*Annalen*, 1909, **370**, 315; 1910, **374**, 121; *Ber.*, 1910, **43**, 596; *Annalen*, 1912, **392**, 235; 1913, **401**, 121; 1918, **415**, 232; *J. pr. Chem.*, 1921, **103**, 1; *Annalen*, 1925, **442**, 93; **445**, 92). Thus in the dichlorohydrocarbon mentioned, one Cl is the potentially mobile anion, and the other functions like Cl in the *p*-chlorophenyl compounds referred to on p. 909.

EXPERIMENTAL.

α-Phenylallyl alcohol was obtained from acraldehyde and magnesium phenyl bromide as described by Moureu and Gallacher (*loc. cit.*). The p-*nitrobenzoate*, obtained (as an oil that solidified) by heating the alcohol (3·9 g.), pyridine (30 c.c.), and *p*-nitrobenzoyl chloride (5·9 g.) on the steam-bath for 15 hours and pouring the product into water, crystallised from alcohol in colourless plates, m. p. 45—46° (Found: C, 68·1; H, 4·7. $C_{16}H_{13}O_4N$ requires C, 67·8; H, 4·6%). Cinnamyl *p*-nitrobenzoate, prepared similarly, has m. p. 77—78° (compare Hill and Nason, *J. Amer. Chem. Soc.*, 1924, **46**, 2215).

Conversion of α-Phenylallyl Alcohol into Cinnamyl Alcohol.—Reference has already been made to our failure to repeat Valeur and Luce's observation of direct interconversion; we used hot and cold sulphuric acid of various dilutions, and cold alcoholic hydrochloric acid, but obtained either unchanged material or products of high and indefinite boiling point. A mixture of α-phenylallyl alcohol (5 g.) and acetic anhydride (5 c.c.) was boiled for 6 hours and then distilled. The acetate had b. p. 135—145°/15 mm., and its identity with cinnamyl acetate was confirmed by hydrolysis to the crystalline alcohol under conditions in which the un-isomerised α-phenylallyl acetate became converted into phenyl ethyl ketone.

It was boiled for 3 hours with 100 g. of 5% alcoholic potassium hydroxide, and the neutral hydrolysis product isolated in the usual way (4·5 g.); 0·5 g. of the ketone was obtained and the remainder was cinnamyl alcohol, b. p. 240—250°, m. p. 33°. A longer period of heating completes the reaction, which is not detectably reversible.

Bromide from α-Phenylallyl and Cinnamyl Alcohols.—This crystalline substance was readily obtained by adding the alcohol to an acetic acid solution of hydrogen bromide, but attempts to achieve the reverse reaction by means of moist silver oxide yielded complex mixtures, b. p. 80—300°/15 mm.; moreover, treatment with silver *p*-nitrobenzoate gave an amorphous solid, and ozonolysis was therefore resorted to. A chloroform solution of the bromide was treated with dry ozone for several days, and the oily ozonide decomposed by boiling with water into benzaldehyde (identified as semicarbazone) and bromoacetaldehyde (identified as bromal hydrate). Formaldehyde was not produced.

α-p-*Tolylallyl Alcohol*, $C_6H_4Me{\cdot}CH(OH){\cdot}CH{:}CH_2$.—The Grignard reagent prepared from magnesium (6 g.), *p*-bromotoluene (43 g.), ether (100 c.c.), and a trace of iodine was cooled below 0° and treated during 1·5 hours with a solution of acraldehyde (14 g.) in ether (72·5 c.c.). The mixture was well stirred for a further 3 hours and then decomposed by ice and dilute acetic acid. The oil obtained after extraction with ether, washing with sodium bicarbonate solution, drying, and evaporation was fractionated, and a fraction (20 g.), b. p. 120—122°/10 mm., collected; the remainder was *pp'*-ditolyl. The p-*nitrobenzoate*, prepared by the pyridine method, separated from alcohol in colourless, glistening plates, m. p. 82° (Found: C, 68·9; H, 5·25. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·09%).

Conversion of α-p-*Tolylallyl Alcohol into* 4-*Methylcinnamyl Alcohol*.—This reaction was carried out as described on p. 914 but took place even more readily, the transformation to 4-methylcinnamyl acetate, b. p. about 140°/10 mm., being complete in 6 hours. The alcohol obtained by hydrolysis of the acetate at once solidified; m. p. 48°. A single crystallisation from ligroin yielded pure 4-*methylcinnamyl alcohol* as colourless, glistening plates, m. p. 51—52° (Found: C, 81·1; H, 8·05. $C_{10}H_{12}O$ requires C, 81·05; H, 8·2%). The p-*nitrobenzoate*, prepared by the pyridine method, crystallised from alcohol in almost colourless, prismatic needles, m. p. 131—132° (Found: C, 68·9; H, 5·2. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·1%).

Bromide from α-p-*Tolylallyl Alcohol* (4-*Methylcinnamyl Bromide*), $C_6H_4Me{\cdot}CH{:}CH{\cdot}CH_2Br$.—The bromide was prepared from the tolylallyl or 4-methylcinnamyl alcohol (8·2 g.) and a glacial acetic acid solution of hydrogen bromide (30%; 50 g.). The bromide (10 g.) separated from acetic acid in colourless, glistening plates, m. p. 64—65° (Found: C, 56·9; H, 5·45. $C_{10}H_{11}Br$ requires C, 56·9; H, 5·25%). When this bromide was treated with silver *p*-nitrobenzoate in cold ethereal solution, an amorphous solid was obtained (Found: C, 66·9; H, 5·7%). The constitution of the bromide was determined by ozonolysis as in the previous example and with corresponding results.

Action of Bromine on αγ-Diphenylallyl Acetate.—αγ-Diphenylallyl alcohol was obtained by the action of cinnamaldehyde on magnesium phenyl bromide, and separated from petrol in long, silky needles, m. p. 58—59° (compare Nomura, *loc. cit.*). The acetate boils at 211°/15 mm. (Nomura gives b. p. 211°/9 mm.).

A solution of the acetate (5·7 g.) in cold carbon tetrachloride was treated with bromine (3·8 g.; a slight excess), also dissolved in carbon tetrachloride. The cold solution slowly deposited a *bromide* (3·9 g.), which crystallised from alcohol in colourless needles, m. p. 176—177° after previous softening (Found: C, 49·7; H, 3·7. $C_{17}H_{16}O_2Br_2$ requires C, 49·5; H, 3·9%). The mother-liquor from this bromide was evaporated to dryness, and the residual viscous oil dissolved in alcohol. A second *bromide* was slowly deposited (3·2 g.), which separated from alcohol in clusters of colourless slender needles, m. p. 122° (Found: C, 49·8; H, 3·95. $C_{17}H_{16}O_2Br_2$ requires C, 49·5; H, 3·9%). The residue (2·15 g.) was a viscous oil.

*γ-Phenyl-α-*p*-tolylallyl Alcohol*, $C_6H_4Me{\cdot}CH(OH){\cdot}CH{:}CHPh$.—The Grignard reagent obtained from magnesium (6 g.), *p*-bromotoluene (43 g.), ether (100 c.c.), and a trace of iodine was treated at the ordinary temperature with a solution of cinnamaldehyde (33 g.) in ether (72·5 c.c.). The mixture was then boiled for 30 minutes and decomposed with ice and dilute acetic acid. The oil obtained from the ethereal extract, after being washed free from acid and dried, partly solidified on standing. After draining, the solid residue (22 g.) crystallised from petrol in colourless needles, m. p. 78—79° (Found: C, 85·7; H, 6·9. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

Conversion into p*-tolyl β-phenylethyl ketone.* This *ketone* was obtained in almost quantitative yield by boiling the alcohol (3·5 g.) with alcoholic 20% potassium hydroxide (100 g.) for 2 hours and pouring the product into water. The oil obtained solidified and, after being washed free from alkali, crystallised from alcohol in glistening plates, m. p. 70° (see p. 920).

*Acetylation of γ-Phenyl-α-*p*-tolylallyl Alcohol. Formation of γ-Phenyl-α-*p*-tolylallyl Acetate and α-Phenyl-γ-*p*-tolylallyl Acetate.*—A mixture of the pure alcohol (m. p. 78—79°) (15 g.) and acetic anhydride (15 c.c.) was boiled for 6 hours. After removal of the excess of acetic anhydride, the residue distilled at 210—211°/11 mm. (Found: C, 80·9; H, 6·75. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%). That this constant-boiling liquid was a mixture of isomeric acetates was proved by hydrolysis and ozonisation.

Conversion into ketones. The acetate mixture (9 g.) and 20% alcoholic potassium hydroxide solution (150 g.) were boiled together for 2·5 hours, the excess of alcohol was then removed, and the residue was poured into water and extracted with ether. The oil (7·3 g.) obtained from the extract yielded *p*-tolyl β-phenylethyl ketone (1·5 g.), m. p. 69—70°; the residual oil solidified below 0°, but immediately liquefied on warming to the room temperature. The latter was oximated in the usual manner, and the resulting liquid mixture of oximes, when kept in a vacuum, deposited a crystalline oxime, which separated from petrol in colourless needles, m. p. 85—86°, identical with phenyl β-*p*-tolylethyl ketoxime (p. 921).

Ozonolysis. A solution of the mixed acetates in chloroform was treated with ozonised oxygen for several days. A considerable amount of *p*-toluic acid separated. The mixture obtained on evaporation of the chloroform was separated by means of ether and sodium carbonate into acid and neutral portions. The former consisted of impure *p*-toluic acid containing benzoic acid, some of which was isolated by sublimation. The neutral material was boiled with water for 1 hour and with 15% hydrochloric acid for 4 hours, and the product again divided into neutral and acid portions, as before. The small neutral portion, on treatment with aqueous semicarbazide acetate, gave an incompletely solid mixture of semicarbazones, from which, on crystallisation from glacial acetic acid, *p*-tolualdehyde semicarbazone was obtained. The mixed acids were rubbed with about twice their weight of cold water. The insoluble portion proved to be *p*-toluic acid containing benzoic acid. The aqueous lixiviate, on concentration, deposited first mandelic acid and then an impure mixture, from which a pure acid could not be isolated on account of the small amount and its great solubility. It was therefore oxidised with warm 3% hydrogen peroxide and sodium carbonate. On acidification, sparingly soluble acids were precipitated which on crystallisation from dilute acetic acid yielded *p*-toluic acid.

Action of Cinnamaldehyde on Magnesium p-*Chlorophenyl Iodide. Formation of* α-*Phenyl*-γ-p-*chlorophenylallyl Alcohol and* γ-*Phenyl*-α-p-*chlorophenylallyl Alcohol.*—The Grignard reagent prepared from magnesium (6 g.), *p*-chloroiodobenzene (60 g.), ether (100 c.c.), and a trace of iodine was treated at the ordinary temperature with a solution of cinnamaldehyde (33 g.) in ether (72·5 c.c.). The mixture was boiled for 30 minutes and then decomposed with ice and dilute acetic acid. The ethereal extract was washed with sodium hydrogen sulphite solution, sodium hydrogen carbonate, and water. The residue from the ether was a viscous oil (54 g.) which could not be distilled.

The mixed acetates, prepared by boiling the mixture of alcohols for 6 hours with acetic anhydride, were obtained as a straw-coloured, viscous oil, b. p. 225—226°/13 mm. (Found: C, 71·4; H, 5·1. $C_{17}H_{15}O_2Cl$ requires C, 71·2; H, 5·3%).

Action of bromine. A solution of the mixed acetates (7·4 g.) in carbon tetrachloride, after treatment with bromine (4·2 g.), slowly deposited a *bromide* (1·1 g.), which separated from alcohol in prismatic needles, m. p. 193—194° (Found: C, 45·65; H, 3·3. $C_{17}H_{15}O_2ClBr_2$ requires C, 45·7; H, 3·4%). The viscous mass obtained after evaporation of the solvent was dissolved in hot alcohol. On cooling, a second *bromide* (1·05 g.) separated, which crystallised from alcohol in colourless prisms, m. p. 180° (Found: C, 45·8; H, 3·4. $C_{17}H_{15}O_2ClBr_2$ requires C, 45·7; H, 3·4%). The residue (9 g.) was a very viscous gum.

Conversion into ketones. A solution of the mixed acetates (10 g.) in 20% alcoholic potassium hydroxide solution (200 g.) was boiled for 2·5 hours, and the neutral product isolated as an oil (7·7 g.). This was boiled for 24 hours with alcohol (50 c.c.), hydroxylamine hydrochloride (2·4 g.), and sodium acetate (2·9 g.). Extraction with ether in the usual manner gave a residue (7·8 g.), which partly solidified in a vacuum. The solid was washed with and crystallised from ligroin. It separated in colourless, slender needles, m. p. 117—118°, and was identical with a synthesised sample of *phenyl* β-p-*chlorophenylethyl ketoxime* (p. 919). The mother-liquor, after evaporation of the solvent, was kept in an evacuated desiccator for several days; further crystallisation then ensued. This solid, after draining, crystallised from ligroin in colourless prisms, m. p. 111—112°, and was identical with a synthesised specimen of p-*chlorophenyl* β-*phenylethyl ketoxime* (p. 920). A mixture of about equal parts of the oximes melted at 86—95°.

Ozonolysis. (a) *The mixed acetates.* A solution of the mixed acetates (7·8 g.) in chloroform was treated with ozonised oxygen for 6 days, the solution being filtered from time to time to remove the precipitated *p*-chlorobenzoic acid (2·8 g.; m. p. 225—235°, unpurified; m. p. and mixed m. p. 235—236°, after crystallisation from dilute alcohol). The acid products in the chloroform yielded 0·09 g. of *p*-chlorobenzoic acid (m. p. 230—235°), 0·79 g. of crude benzoic acid (0·49 g., m. p. 115—120°; 0·30 g., m. p. 112—115°), and a residue, which was boiled with hydrochloric acid for 3 hours; the small residue obtained on evaporation to dryness was heated to 100° to remove benzoic acid and then crystallised from water, mandelic acid being obtained. The neutral product from the chloroform (2·4 g.) was boiled with water for 1 hour and then oxidised at 35—45° with sodium chlorate (0·5 g.) and osmium tetroxide (0·05 g.) in the presence of a little sodium carbonate. The neutral portion of the oxidation product, probably unoxidised material, was small and was not further examined. The acid portion was separated by means of water into a sparingly soluble mixture of acids (small quantity), which on crystallisation from chloroform yielded *p*-chlorobenzoic acid, and a mixture of very soluble acids (main portion). The chloroform solution contained benzoic acid (sublimation). The soluble acids yielded mandelic acid, and a second substance which could not be isolated in the pure condition. It was therefore oxidised with warm 6% hydrogen peroxide and sodium carbonate; on acidification, *p*-chlorobenzoic acid and benzoic acid were obtained.

(b) *The mixed alcohols.* This experiment was carried out like the preceding one with results which were substantially identical both qualitatively and quantitatively.

Preparation of Reference Ketones.

Ethyl p-*Chlorobenzylbenzoylacetate,* $C_6H_5{\cdot}CO{\cdot}CH(CH_2{\cdot}C_6H_4Cl){\cdot}CO_2Et$.—An alcoholic solution of ethyl sodiobenzoylacetate prepared from sodium (1·44 g.), ethyl alcohol (20 g.), and ethyl benzoylacetate (12 g.) was boiled for 2 hours with a solution of *p*-chlorobenzyl bromide (12·85 g.) in alcohol (30 c.c.). The product was isolated in the usual way as a colourless, viscous oil, b. p. 240°/12 mm., which later solidified and then crystallised from alcohol in needles, m. p. 54—55° (Found: C, 67·9; H, 5·5. $C_{18}H_{17}O_3Cl$ requires C, 68·2; H, 5·4%).

Phenyl β-p-*chlorophenylethyl ketone,* $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl$, was obtained by hydrolysing the above ester with dilute sulphuric acid or barium hydroxide. It separated from alcohol in colourless needles, m. p. 58° (Found: C, 73·6; H, 5·6. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·4%). The *oxime*, prepared in the usual manner, crystallised from ligroin in colourless, slender needles, m. p. 117—118° (Found: C, 69·6, 69·5; H, 5·5, 5·5; N, 5·5, 5·55; Cl, 13·6, 13·75. $C_{15}H_{14}ONCl$ requires C, 69·4; H, 5·4; N, 5·4; Cl, 13·6%).

Ethyl p-*Chlorobenzoylacetate,* $C_6H_4Cl{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$.—A solution of ethyl acetoacetate (26 g.) in alcoholic sodium ethoxide prepared from sodium (4·6 g.) and alcohol (35 g.) was treated below 10° with *p*-chlorobenzoyl chloride (17·5 g.). The mixture was then stirred for 30 minutes, and treated in the same way with half the amounts of sodium ethoxide solution and *p*-chlorobenzoyl chloride originally used. Further additions of still smaller quantities were made in like manner and after the use of sodium ethoxide equivalent to 9·2 g. of sodium, and of 35 g. of the chloride, the mixture was kept for 24 hours and then mixed with ether. The crystals obtained were suspended in water (260 c.c.) and shaken at 40—45° for 20 minutes with ammonium chloride (12 g.) and 10% ammonia (40 c.c.). Extraction with ether gave 32 g. of a pale yellow oil, which on distillation yielded a fraction (20 g.), b. p. 175—185°/15 mm. *Ethyl* p-*chlorobenzoylacetate* boils at 181—182°/18 mm., and solidifies to a mass of needles, m. p. 36° (Found: Cl, 15·5. $C_{11}H_{11}O_3Cl$ requires Cl, 15·65%).

Ethyl benzyl-p-*chlorobenzoylacetate*, $C_6H_4Cl{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}CO_2Et$, was obtained from ethyl *p*-chlorobenzoylacetate and benzyl bromide in an analogous manner to its isomeride. It distilled at 228—233°/14 mm., and solidified to a crystalline mass, which separated from alcohol in clusters of colourless needles, m. p. 65° (Found: C, 67·8; H, 5·5. $C_{18}H_{17}O_3Cl$ requires C, 68·2; H, 5·4%).

p-*Chlorophenyl* β-*phenylethyl ketone*, $C_6H_4Cl{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph$, was obtained in colourless, glistening plates, m. p. 78° (from alcohol) by hydrolysis of the above ester with barium hydroxide (Found: C, 72·9; H, 5·3. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·4%). The *oxime* separates from ligroin in small, colourless prisms, m. p. 111—112° (Found: C, 69·4, 69·5; H, 5·5, 5·55. $C_{15}H_{14}ONCl$ requires C, 69·4; H, 5·4%).

Ethyl *p*-toluoylacetate, $C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, was prepared in a similar manner to the corresponding *p*-chloro-compound from ethyl acetoacetate (27 g.), sodium (9·5 g.), ethyl alcohol (160 c.c.), and *p*-toluoyl chloride (35 g.). It boiled at 172—173°/14 mm. Marguery (*Bull. Soc. chim.*, 1905, **33**, 549) gives b. p. 170°/30 mm. (Found: C, 69·7; H, 6·8. Calc.: C, 69·9; H, 6·8%).

Ethyl benzyl-p-*toluoylacetate*, $C_6H_4Me{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}CO_2Et$, was prepared from sodium (1·15 g.), ethyl alcohol (25 c.c.), and ethyl *p*-toluoylacetate (10·3 g.), and benzyl bromide (8·5 g.) dissolved in alcohol (25 c.c.). It was distilled at 232—233°/11 mm. (Found: C, 77·0; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%). On hydrolysis with baryta, *p*-tolyl β-phenylethyl ketone, m. p. 70°, was obtained (compare Mailhe, *Bull. Soc. chim.*, 1914, **15**, 325). The *oxime* separated from ligroin in colourless, glistening plates, m. p. 101—102° (Found: C, 80·5; H, 7·2. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%).

Ethyl p-*methylbenzylbenzoylacetate*,

$$C_6H_5{\cdot}CO{\cdot}CH(CH_2{\cdot}C_6H_4Me){\cdot}CO_2Et,$$

was obtained as a colourless, fairly mobile oil, b. p. 223—225°/10 mm., from ethyl benzoylacetate and *p*-xylyl bromide (Found: C, 76·4; H, 6·4. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%). On hydrolysis with barium hydroxide *phenyl* β-p-*tolylethyl ketone* was isolated as a low-melting, waxy solid. On oximation *phenyl* β-p-*tolylethyl ketoxime*, m. p. 85—86°, colourless needles from ligroin, was obtained (Found: C, 80·3; H, 7·3. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%).

The authors wish to record their thanks to Mr. A. Rumfitt for carrying out the majority of the analyses, and to the Royal Society for a grant with which part of the cost of this investigation has been defrayed.

THE UNIVERSITY, LEEDS. [*Received, February 6th,* 1928.]