

4. *The Modes of Addition to Conjugated Unsaturated Systems. Part IX. A Discussion of Mechanism and Equilibrium, with a Note on Three-carbon Prototropy.*

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The discussion given in the preceding paper, particularly of the kinetic and thermodynamic control of anionotropic rearrangement, and of the significance of conjugation and hyperconjugation energy in anionotropic equilibria, is supplemented by an analogous discussion of prototropic rearrangements in three-carbon systems, and of their equilibria; and the whole of this theory is applied in a consideration of the modes of addition of both electrophilic and nucleophilic addenda to conjugated unsaturated systems. New forms of hyperconjugation in normal molecules are recognised.

THE theory of Organic Chemistry has greatly advanced since 1928, when Part I of this series was written, which mapped the field of the succeeding experimental researches (Parts II—VIII). The subject of additions to conjugated polyenes can therefore advantageously be again reviewed. First, though it is a formal matter, we modernise the originally given classification of addenda, commencing with the explanation that we shall deal here only with heterolytic addition reactions, though sufficient concerning homolytic addition is now known (thanks largely to Kharasch) to encourage an attempt to treat that part of the subject more comprehensively

* A good review of the subject of hyperconjugation is now available (Deasy, *Chem. Reviews*, 1945, 36, 145).

than hitherto. We shall here consider, however, only the following classes of heterolytic addenda :

Electrophilic Addenda :

- (1) Hydrogen halide type (includes ROH_2^+ , *i.e.*, water or alcohol adding under acid catalysis; includes also NOCl).
- (2) Halogen type.

Nucleophilic Addenda :

- (3) Hydrogen cyanide type (includes malonic esters and Michael addenda generally; also water or alcohol adding under alkaline catalysis).
- (4) Hydrogen type.

The fundamental change in our attitude is that, whereas, when Part I was written, so little was known of the constitutional factors of molecular energy that the discussion of orientation had to be based on inescapably qualitative considerations concerning structural effects in the relative rates of alternative reactions, now that conjugation and hyperconjugation are recognised as sources of energy contributions, which can sometimes be independently estimated, it is possible to re-express the matter in terms of the relative energies of alternative products, and thus in terms suitable to later quantitative development. When it is necessary to discuss the kinetic, as distinct from the thermodynamic, control of orientation, we can preserve the same point of view by discussing structural effects on the energies of transition states, even though one is in this case further from the possibility of quantitative treatment.

(a) *Addition of Hydrogen Halides.*—Burton and Ingold sought to show (Part I, *J.*, 1928, 910), and their arguments have been generally accepted, that the addition of hydrogen halides to olefins in solution is normally a two-stage process, which is initiated by the donation of a proton to the olefin by the electrophilic hydrogen halide molecule, and is completed by the neutralisation of the formed carbonium ion through the uptake of a halide ion. In additions to a conjugated polyene the intermediate carbonium ion is, of course, mesomeric, having therefore two or more possible positions for neutralisation in the final stage of the addition.

The initial proton uptake must occur at an end of the conjugated system of a polyene, this being the position in which the greatest negative polarisation can be developed in the transition state of the reaction. If the two ends of such a system are rendered non-equivalent by aryl or alkyl substitution, that end will be preferred as the point of initiation which is also an end of a conjugated or hyperconjugated system involving the substituent. If on account of poly-substitution two non-equivalent ends both fall within this definition, the conjugated or hyperconjugated system involving the most polarisable substituent will control the point of attack. Thus initiation (*) occurs at C_α in β -methylbutadiene and at C_δ in α -phenylbutadiene and α -phenyl- β -methylbutadiene :



Supposing the ions of an anionotropic system to have been formed in the initial reaction stage, it remains to consider their union to give the alternative addition products. At the outset this union must be kinetically controlled. Too little is known concerning transition states of ionisation to permit of any very specific predictions concerning the relative rates of production of the isomeric molecules from these pre-formed ions. However, two general statements may be made. One is that the thermodynamically less stable isomeride should be first formed in more than its equilibrium proportion. This is our general experience with anionotropic systems (preceding paper, p. 11), and it is to some extent made plausible by the consideration that a predisposition must exist for the free energy difference between the isomeric molecules to become reduced in the corresponding transition states of their ionisation, these states being stages on the way to the same pair of ions. The other statement is that the kinetically determined proportions of isomerides are likely to be more sensitive to solvent influence than are their equilibrium proportions. This follows from the expected greater solvation energy of the quasi-ionic transition states, than of the fully formed neutral molecules. Even when we cannot make a comparison of the kinetic and thermodynamic solvent influence, we may still expect great sensitivity to solvent influence in the cases in which the proportions of isomerides are kinetically determined. These principles apply, of course, not only to additions of hydrogen halides but also to those of halogens, and illustrations will be given in relation to both these kinds of addition.

We commence with the least mobile anionotropic systems in order to isolate the effect of kinetic control. Anionotropic chlorides are always less mobile than corresponding bromides. Butadiene itself will produce less mobile systems by addition than any alkyl- or aryl-substituted butadiene or higher polyene. Three hydrochlorides of butadiene can be formulated, but one is theoretically excluded by the principle of terminal initiation; the other two are γ -methylallyl (crotyl) chloride, $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (the α -hydro- δ -chloride), and α -methylallyl chloride, $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}\cdot\text{CH}_2$ (the α -hydro- β -chloride). The addition has been investigated by Kharasch, Kritchevsky, and Mayo (*J. Org. Chem.*, 1937, **2**, 489), who failed to detect the presence of any product other than these two. The proportion of γ -methylallyl chloride formed was 20—25%. This proportion was independent of the temperature between -80° and $+25^\circ$, and the isolated chlorides underwent no measurable conversion under the conditions of their formation. However, prolonged treatment with hydrogen chloride at the upper end of the temperature range caused conversion finally into an equilibrium mixture containing about 75% of γ -methylallyl chloride. Obviously the thermodynamically less stable α -methylallyl chloride is first produced in much more than its equilibrium proportion.

With hydrogen bromide as the addendum a more mobile anionotropic system is produced. The same authors obtained the kinetically controlled mixture of products, containing 20% of γ -methylallyl bromide, only at low temperatures, and with the careful exclusion of oxidant catalysts. At higher temperatures, and especially in the presence of such catalysts, much larger proportions of γ -methylallyl bromide were obtained; and, consistently, in these conditions the isolated bromides underwent facile interconversion to produce the equilibrium mixture, which, according to Winstein and Young's determination (*J. Amer. Chem. Soc.*, 1936, **58**, 104), contains 87% of γ -methylallyl bromide at 25° . Equilibrium proportions of the order of those found for chlorides and bromides are, as we have seen, consistent with the principles outlined in the preceding paper.

An interesting variant of these phenomena arises in the case of vinylacetylene. Carothers, Berchet, and Collins have shown (*J. Amer. Chem. Soc.*, 1932, **54**, 4066) that the initial product of addition of hydrogen chloride contains a large proportion of chloromethylallene, $\text{CH}_2\cdot\text{C}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (an α -hydro- δ -chloride with the added hydrogen at the acetylene end), which in the presence of hydrogen chloride or cuprous chloride rearranges completely to yield chloroprene, $\text{CH}_2\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}_2$ (the corresponding α -hydro- β -chloride). Initiation only at the acetylenic end of this molecule accords with the principle (Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 909) that in such a case the electrons will concentrate preferentially towards the *more* unsaturated end. The proportions of the tautomerides at equilibrium will be determined partly by the (negative) butadienoid resonance energy of chloroprene, probably about 6 kilocal., and partly by the (positive) "strain" energy of the chloromethylallene, probably about 8 kilocal.; obviously, therefore, chloroprene should be formed to the complete exclusion of the allene derivative. But initially the thermodynamically labile isomeride is produced in considerable proportion, consistently with the general principle given above.

For substituted butadienes the number of possible isomeric hydrohalides is three or six according as the system is symmetrical or not. Our knowledge of the effect of the phenyl group in promoting the mobility of anionotropic systems shows that in the case of phenyl-substituted butadienes there will be hardly any possibility of isolating either hydrobromides or hydrochlorides out of equilibrium. This being so, the principles governing the terminal initiation of addition, and the dominating energy effect of phenyl-vinyl conjugation, together should secure the production of a single isomeride in most cases, *e.g.*,



In the case of α -phenylbutadiene, the exclusive formation of the expected δ -hydro- γ -bromide has been established by Riiber (*Ber.*, 1911, **44**, 2977), and of the corresponding δ -hydro- γ -chloride by Muskat and Huggins (*J. Amer. Chem. Soc.*, 1934, **56**, 1239).

The methyl-substituted butadienes will produce less mobile addition products than their phenyl analogues, but we may expect that it will be difficult to isolate hydrobromides out of equilibrium, although the corresponding task with hydrochlorides should prove comparatively easy. Most of the recorded investigations relate to additions of hydrogen bromide. With β -methylbutadiene we expect α -initiation, and this must lead to the already discussed system

consisting of $\gamma\gamma$ - and $\alpha\alpha$ -dimethylallyl bromides, $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and $\text{CH}_3\cdot\text{CMeBr}\cdot\text{CH}\cdot\text{CH}_2$ (preceding paper, p. 12). Here the $\gamma\gamma$ -isomeride is much the more thermodynamically stable owing to the doubled methyl hyperconjugation; and consistently, Claisen has shown (*J. pr. Chem.*, 1922, **105**, 65; cf. Farmer and Marshall, *J.*, 1931, 139) that the product of addition of hydrogen bromide to isoprene consists exclusively of $\gamma\gamma$ -dimethylallyl bromide. Hydrogen chloride has been shown to add in the same way (Jones and Chorley, *J.*, 1946, 832). $\beta\gamma$ -Dimethylbutadiene is a closely similar example since the extra methyl group has a like effect on both isomerides, $\text{CH}_3\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ and $\text{CH}_3\cdot\text{CMeBr}\cdot\text{CMe}\cdot\text{CH}_2$, of the formed anionotropic system; and correspondingly, Claisen and Farmer and Marshall have established (*loc. cit.*) that the sole product of the addition of hydrogen bromide to this hydrocarbon is $\beta\gamma\gamma$ -trimethylallyl bromide (*loc. cit.*).

A less black-and-white picture is presented by $\alpha\delta$ -dimethylbutadiene. In this case the same authors proved that both the isomerides which are rendered possible by the terminal initiation of addition are obtained in the proportions here indicated :



Assuming equilibrium, the preponderance of an α -hydro- β -bromide is to be expected, because we have to balance the energy effects of hyperconjugation by methyl in the one isomeride and by ethyl in the other, and, as Baker has shown both theoretically and practically, the former effect is the greater. Taking the differential energy effect a 0.4 kilocal. (from the differences in the heats of hydrogenation of but-2-ene and pent-2-ene), the equilibrium proportions at the experimental temperature are calculated to be 70% : 30%. The agreement is more than sufficient, since in using so small an energy difference we are almost certainly making the calculation dependent on a quantity which is of the same order of magnitude as the quantities neglected.

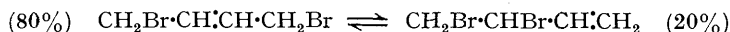
(b) *Additions of Halogens.*—Since the date of Burton and Ingold's paper a valuable discussion of the mechanism of halogen addition to simple olefins has been given by G. Williams (*Trans. Faraday Soc.*, 1941, **37**, 749). His discussion confirms the view that the simplest mechanistic conditions arise in strongly ionising, especially in aqueous, solvents. The addition then consists of the electrophilic attack of the halogen molecule on one of the unsaturated carbon atoms, followed by a neutralisation of the formed carbonium ion through the uptake of a halide ion. Williams also draws attention, however, to the evidence, which was even at that date beginning to accumulate, largely through the work of Robertson and his collaborators, that in less ionising and non-ionising solvents halogen addition is markedly multiform. The continuing researches of Robertson have now brought to light a number of homogeneous mechanisms, quite apart from the heterogeneous processes which may occur on suitable surfaces in the presence of non-polar solvents. The kinetically distinguished homogeneous processes include (i) second-order chlorine- and bromine-addition with rate proportional to [olefin][hal₂], (ii) third-order bromine addition (but not chlorine addition) with rate proportional to [olefin][Br₂]², (iii) fourth-order bromine (but not chlorine) addition with rate proportional to [olefin][Br₂]³. All these reactions are shown to be electrophilic, but it is by no means certain that they all involve an intermediate having a carbonium ionic centre, though Williams has suggested that the third-order reactions may do so. It is not necessary to enumerate here the additional electrophilic mechanisms involving special homogeneous catalysts; most of these can probably be accommodated in an extension of White and Robertson's original formulation of such reactions (*J.*, 1939, 1509; cf. Williams, *loc. cit.*; Swedlund and Robertson, *J.*, 1945, 131; *J.*, 1947, 630; de la Mare, Scott, and Robertson, *J.*, 1945, 509; Waters, Caverhill, and Robertson, *J.*, 1947, 1168). All the above-mentioned mechanisms seem to us likely to play some part in the applications to conjugated systems with which we shall be concerned, though no kinetic studies of halogen addition to conjugated polyenes are yet available to support this assumption. We shall not need to refer here to the group of *nucleophilic* halogen additions, which apply to $\alpha\beta$ -unsaturated carbonyl and nitro-compounds in conditions of hydrogen-ion catalysis (Morton and Robertson, *J.*, 1945, 129; de la Mare and Robertson, *J.*, 1945, 888; Ting and Robertson, *J.*, 1947, 628).

In additions to conjugated polyenes the precise mechanism will, of course, affect the immediate, kinetically determined ratio in which the isomeric addition products are formed, but not the ultimate, thermodynamically determined ratio. Where the mechanism involves an intermediate having a carbonium-ion centre, this will be the cation of an anionotropic system, and the kinetically controlled product ratio will depend on the relative rates of uptake of an anion in the alternative possible positions. In this case, if a phase of kinetic control can be distinguished, we may expect an initial production of more than the equilibrium proportion of

the thermodynamically less stable isomeride, and this proportion is likely to be very sensitive to the solvent. In other cases the kinetically controlled product ratio will depend on the exact mechanism in ways which cannot be predicted in detail, but may be assumed to depend closely on stereochemical considerations. The possibility is therefore not excluded that the thermodynamically more stable isomeride might in special cases be formed initially in more than its equilibrium proportion.

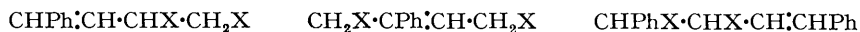
For the purpose of considering the thermodynamic control of product proportions, we shall have to take explicit account of an energy term which could be neglected in the cases previously discussed, not because its absolute value was likely to be particularly small, but because it was always balanced in the isomerides under consideration: such balancing no longer obtains in anionotropic products formed by halogen addition. We refer to the hyperconjugation energy associated with the system $\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}-\text{Hal}$, a sort of counterpart of the hyperconjugation energy which Baker and Nathan recognised in the system $\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}-\text{H}$. We think that a third type of hyperconjugation, *viz.*, that of the system $\text{H}-\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}-\text{Hal}$, is also of energetic importance for normal molecules. Some evidence for this seems recognisable in the data of Conn, Kistiakowsky, and Smith for the heats of addition of bromine to simple olefins (*J. Amer. Chem. Soc.*, 1938, 60, 2764).

We may expect that amongst the least mobile anionotropic systems that can be produced by the addition of halogens to polyenes will be those which are derived from butadiene itself, and that the dichloride of butadiene will be less mobile than the dibromide. The addition of chlorine to butadiene has been investigated by Muskat and Northrop (*J. Amer. Chem. Soc.*, 1930, 52, 4043), who found the $\alpha\beta$ -dichloride to preponderate over the $\alpha\delta$ -isomeride in the ratio of about 2 : 1. The dichlorides underwent no interconversion under the conditions of their formation; and, indeed, the authors failed to interconvert them, although this could, no doubt, be accomplished by the aid of appropriate solvents or catalysts. We must regard the proportions as kinetically determined, since we should expect the $\alpha\delta$ -isomeride to be the principal constituent of the mixture at equilibrium. The addition of bromine to butadiene has been investigated by several authors, but most thoroughly by Farmer, Lawrence, and Thorpe (*J.*, 1928, 729), who, in a series of solvents ranging from hexane to acetic acid, obtained dibromide mixtures containing from 38% to 70% of the $\alpha\delta$ -isomeride. Some interconversion of isomerides in the sense $\alpha\beta \rightarrow \alpha\delta$ could be detected in the conditions of the addition, but such isomerisation was too slow to be made responsible for the formation of more than a very small proportion of the $\alpha\delta$ -compound produced by addition. Conversion of the isolated isomerides into an equilibrium mixture was effected, and the mixture then contained about 80% of the $\alpha\delta$ -dibromide, a figure which Muskat and Northrop have confirmed. These results illustrate both the sensitivity of the kinetically-controlled product ratio to solvent influences, and the initial production of an excessive proportion of the thermodynamically less stable isomeride. We attribute the greater thermodynamic stability of the $\alpha\delta$ -compound mainly to the circumstance that the energy effect of its doubled bromine hyperconjugation is greater than that of the single hyperconjugation of the same kind in the $\alpha\beta$ -isomeride:



The only other known cases in which a phase of kinetic control has been detected as a precursor to the formation of products in equilibrium are those of *cyclopentadiene* and *cyclohexadiene*, from which mixtures containing 1 : 2-dibromides are first formed, although in the readily attained equilibria the main product is the 1 : 4-compound (see below).

With phenyl-substituted butadienes we may expect to obtain only equilibrium products in additions of either bromine or chlorine. This being so, the principle of terminal initiation, and the dominating energy effect of phenyl-vinyl conjugation, will in most cases determine the exclusive formation of a single addition product. Thus α -phenylbutadiene should yield a $\gamma\delta$ -dihalide, β -phenylbutadiene an $\alpha\delta$ -dihalide, and $\alpha\delta$ -diphenylbutadiene an $\alpha\beta$ -dihalide:



Muskat and Northrop (*loc. cit.*) have experimentally established the exclusive formation from α -phenylbutadiene of the $\gamma\delta$ -dichloride, and Straus that of the $\gamma\delta$ -dibromide (*Ber.*, 1909, 42, 2867). Straus has also shown that $\alpha\delta$ -diphenylbutadiene forms only the $\alpha\beta$ -dibromide. The rule is that phenyl-vinyl conjugation will always be preserved to the greatest possible extent. A closely analogous case is that of hexatriene, in which a dominating tendency to the preservation

of butadienoid conjugation should determine $\alpha\beta$ - and $\alpha\zeta$ -addition to the exclusion of $\alpha\delta$ - and $\gamma\delta$ -addition. The addition of bromine to hexatriene has been investigated by Farmer, Laroia, Switz, and Thorpe (*J.*, 1927, 2937), who were able to isolate only the $\alpha\beta$ - and $\alpha\zeta$ -dibromides $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ and $\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$.

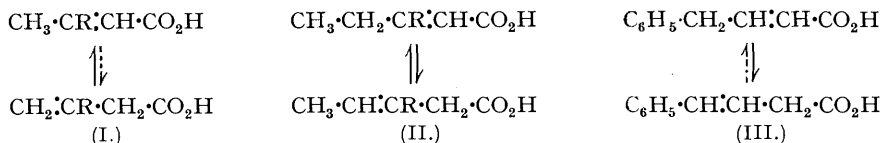
In β - and γ -alkylated butadienes we see the tendencies already illustrated with respect to butadiene reinforced by alkyl hyperconjugation; and, since the thermodynamically less stable addition compound is necessarily a tertiary halide, we may expect only equilibrium products in the addition of bromine; they would probably be difficult to avoid in the addition of chlorine under ordinary conditions. Thus in β -methylbutadiene the initiation of addition at C_α excludes $\gamma\delta$ -addition, and of the remaining possible addition products only the $\alpha\delta$ -compound, $\text{CH}_2\text{X}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\text{X}$, preserves the hyperconjugation of the methyl group. Since halogen hyperconjugation works in the same direction, we may be sure that the $\alpha\delta$ -dihalides will preponderate at equilibrium. Jones and Williams have shown (*J.*, 1934, 829) that the dichloride obtained from isoprene consists essentially of the $\alpha\delta$ -compound, although indications were obtained of the formation of a second isomeride in small amount. The dibromide of isoprene has also been shown to consist essentially of the $\alpha\delta$ -compound (Bergmann, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 1885; Staudinger, Muntwyler, and Kupfer, *Helv. Chim. Acta*, 1922, 5, 756). The case of $\beta\gamma$ -dimethylbutadiene is essentially similar, the extra methyl group having a like effect on the stability of each of the formed dihalides. Accordingly, it has been found that the dibromide of this hydrocarbon consists mainly of the $\alpha\delta$ -compound, $\text{CH}_2\text{Br}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ (Kondakow, *J. pr. Chem.*, 1900, 62, 166; Macallum and Whitby, *Trans. Roy. Soc. Canada*, 1928, iii, 22, 33; Farmer, Lawrence, and Scott, *J.*, 1930, 510; Sweeting and Johnson, *J. Amer. Chem. Soc.*, 1946, 68, 1057). $\alpha\gamma$ -Dimethylbutadiene is another case in which an equilibrium product should be readily formed. Here the initiation of reaction at C_β excludes the $\alpha\beta$ -dihalide, and, as regards the remaining possibilities, the effect of methyl hyperconjugation should be roughly balanced (although the methyl groups are not strictly equivalent), whilst halogen hyperconjugation should favour the $\alpha\delta$ -isomeride. The addition of bromine has been investigated, and the $\alpha\delta$ -dibromide, $\text{CHMeBr}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$, has been proved to be the principal product (Farmer, Lawrence, and Scott, *loc. cit.*).

Three terminally dialkylated butadienes have been studied with respect to the mode of addition of bromine, namely $\alpha\delta$ -dimethylbutadiene (Duden and Lemme, *Ber.*, 1902, 35, 1338; Farmer, Lawrence, and Scott, *loc. cit.*), cyclopentadiene (Thiele, *Annalen*, 1900, 314, 296; Farmer and Scott, *J.*, 1929, 172), and cyclohexa-1:3-diene (Farmer and Scott, *loc. cit.*). In these cases the anionotropic systems formed by addition are expected to be somewhat less mobile than those considered in the preceding paragraph. In the examples of cyclopentadiene and cyclohexa-1:3-diene the formation of mixtures of dibromides which are distinctly out of equilibrium has been observed by Farmer and his collaborators. In all three cases the equilibrium product consists essentially of the 1:4-dibromide. The prediction of these equilibria is at present impossible, since it involves the setting-off of the effect of methyl or methylene hyperconjugation in the 1:2-dihalide against that of an extra halogen hyperconjugation in the 1:4-isomeride, and we have no independent data by which these effects can be weighted relatively to each other. On general grounds it seems probable that the energy effect of halogen hyperconjugation will be rather strongly dependent on whether the halogen is in primary, secondary, or tertiary combination.

(c) *Note on Three-carbon Prototropy.*—Just as the preceding consideration of the behaviour of electrophilic addenda towards conjugated systems required reference to the theory of anionotropic systems, so the discussion still to be given of nucleophilic addenda will involve reference to the chemistry of prototropic systems. As we are not submitting a paper on prototropy at the present time, it is needful to include here some remarks on those aspects of the subject which we shall require for application in the last sections of this paper.

One such aspect relates to so-called "three-carbon" systems in equilibrium. These systems are propenes carrying at least one unsaturated end-group of "activating" character, such as COR , CO_2R , COCl , CO_2^- , or CN . Most of the data for the equilibria of these systems we owe to Kon and Linstead. These data were once collated and discussed by one of the present authors (*Ann. Reports*, 1927, 24, 109—113; cf. *ibid.*, 1928, 25, 119), but this was before conjugation and hyperconjugation energy were recognised, and the correlation could not, therefore, be put upon the basis of energy relations; which is not only the right basis for future development, but is also the best one for present application. We therefore here present the matter in a revised form: what we shall say is in part a translation, in part a correction, of the older discussion.

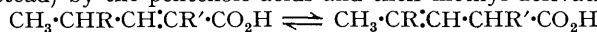
The observations may be grouped as follows. In three-carbon systems with a single activating group, the equilibrium between the $\alpha\beta$ - and the $\beta\gamma$ -unsaturated forms is not particularly sensitive to the nature of the activating group, but is highly sensitive to substitution in certain positions in the three-carbon system itself. Whenever the γ -position (*every* γ -position if there is more than one) is unsubstituted, as in crotonic, $\beta\beta$ -dimethylacrylic, or β -methylcinnamic acids (I; R = H, Me, Ph)—many other examples could be given—the form exclusively present at equilibrium is the $\alpha\beta$ -unsaturated form. As the mentioned examples show, the replacement of β -hydrogen by β -methyl, or even by β -phenyl, makes no difference to this result. However, the introduction of a single γ -methyl group shifts the balanced reaction towards the side of the $\beta\gamma$ -unsaturated isomeride, which now becomes always an important, and often the preponderating form at equilibrium (II). A γ -phenyl group has a larger effect in the same direction (Bougeault), the $\beta\gamma$ -isomeride being now the exclusive form at equilibrium (III):



On the other hand, higher γ -alkyl groups are less effective than γ -methyl as is shown by the following results (Kon and May) relating to the acids $(\text{R}\cdot\text{CH}_2)_2\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and their isomerides (IV; R = H, Me, Et, Pr $^\beta$):

γ -Substituent (R)	H	CH ₃	CH ₂ -CH ₃	CH(CH ₃) ₂
$\beta\gamma$ -Form at equilibrium	0%	95%	67%	51%

Finally, there is evidence that, just as γ -methyl groups shift equilibria so as to favour the $\beta\gamma$ -unsaturated forms, so α -methyl substituents shift them in the opposite direction, as is illustrated (Goldberg and Linstead) by the pentenoic acids and their methyl derivatives,



V; R, R' = H, Me):

Acids	γ -Methylpentenoic	Pentenoic	α -Methylpentenoic
$\beta\gamma$ -Form at equilibrium.....	94.4%	24.6%	19.3%

The theory of these relationships is as follows. The non- γ -substituted compounds, such as (I), exist at equilibrium practically entirely in the $\alpha\beta$ -form, because the (negative) conjugation energy of the olefinic bond with the activating group contributes to the free energy of this form, whilst the $\beta\gamma$ -form possesses no compensating constitutional energy term conferred on it by the special position of its double bond. β -Substituents conjugate or hyperconjugate with the double bond in either position and therefore have only second-order effects on the energy difference which determines the equilibrium. In the γ -methyl compounds (II), the conjugation energy in the $\alpha\beta$ -form is compensated to a considerable extent in the $\beta\gamma$ -form by the hyperconjugation energy of the γ -methyl group with the $\beta\gamma$ -double bond. In γ -phenyl compounds (III), there is an over-compensation in the same sense, due to the large resonance energy of phenyl-to-vinyl conjugation (this vol., p. 16). It is a characteristic of alkyl hyperconjugation (indeed, it is the property which led Baker and Nathan to discover the phenomenon) that the methyl group is more effective than ethyl, and still more than *isopropyl*, and so on: $\text{H} \ll \{\text{Me} > \text{Et} > \text{Pr}^\beta > \text{Bu}^{\text{tert}}\}$. Thus we can readily understand the observed order of alkyl effects as illustrated in series (IV). Finally, it is obvious that, just as γ -methyl hyperconjugates with the $\beta\gamma$ -double bond, so an α -methyl group will hyperconjugate with the $\alpha\beta$ -double bond, but less strongly, because this effect competes with the conjugation between the same double bond and the activating group. Thus can be understood the data illustrated in series (V).

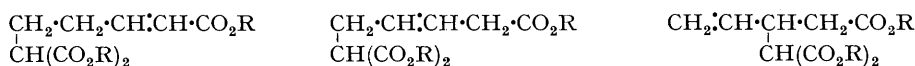
In addition to activated systems such as these, we shall have occasion to consider true three-carbon systems, *i.e.*, propene systems not terminated by unsaturated groups of high electron-affinity. These systems cannot dissociate into ions under the relevant experimental conditions, but we shall be concerned with their formation, irreversibly, and out of thermodynamic equilibrium, from ions which have been produced by addition. Even here, however, we shall maintain an analogous point of view by considering the effect of conjugation and hyperconjugation energy on the alternative transition states of ionic recombination, remembering that, as has already been discussed in other cases, we may generally expect to obtain more than the equilibrium amount of the thermodynamically less stable isomeride.

(d) *Addenda of the Hydrogen Cyanide Type*.—The reactions of these addenda are all base-catalysed, with the main activation barrier in the first stage; which consists of the addition of a nucleophilic anion, such as OMe^- , CN^- , $\text{CH}(\text{CO}_2\text{Me})_2^-$, etc., to a positively polarisable position in a conjugated system terminated by at least one unsaturated, electron-attracting group, such as COR , CO_2R , CN , etc. The addition is strongly reversible: often, under the conditions of preparative work, the rates of formation of the addition product, and of its dissociation into its factors, are of quite the same order of magnitude. In additions to butadiene derivatives the β - and δ -positions with respect to the activating group are both positively polarisable, and we shall be largely concerned with the question of which of them receives, and succeeds in holding, the anionic addendum.

The addition product of the first stage of reaction is an anion, which in the second stage unites with a proton. Further, the product of the first stage is the anion of a prototropic system, so that there are generally alternative final products, differing in the position of a proton. However, we shall most fully discuss the first stage, which determines the carbon framework of the final addition product. The principles governing the second stage of addition are essentially those outlined in the preceding section (c).

There can be no doubt that if the direction of the first stage addition process were kinetically controlled, *i.e.*, if the anionic addition product could not again dissociate, the addition to a butadiene chain with an appropriate end-group would be substantially terminal; *i.e.*, the δ -position in the system would receive the adding anion. The reason is the same as that given for terminal initiation in the addition of electrophilic reagents, such as chlorine or hydrogen chloride, to butadienes: polarity in a freely conducting, linear system is necessarily developed at its ends. The difference between the two cases is that the group of nucleophilic additions now under consideration are more prone to, and have more opportunity for, reversal. However, we may venture the prediction that if, in order to exclude effects due to reversibility, we should isolate a Michael addition product, *e.g.*, of methyl malonate to methyl sorbate, $\text{CH}_3\text{:CH:CH:CH:CH}\cdot\text{CO}_2\text{Me}$, or of methyl cyanoacetate to methyl γ -methylsorbate, after an indefinitely small amount of reaction, the addition product would consist substantially of the esters formed by addition in the δ -position only. The compositions would thus be quite different from those of the products of the same reactions allowed to run to equilibrium (see below). Naturally this applies only if the conjugated system stops at the δ -position.

However, in preparative work, the additions are usually allowed to run to equilibrium, and hence, in seeking an interpretation of existing observations, it is necessary to consider the direction of addition as thermodynamically controlled, *i.e.*, as dependent solely on the relative free energies of the end-products. For the addition, *e.g.*, of malonic esters to β -vinylacrylic esters, $\text{CH}_2\text{:CH:CH:CH}\cdot\text{CO}_2\text{R}$, there are two possible, prototropically related, end-products of δ -addition, and one end-product of β -addition:



The observations, a large proportion of them due to Farmer, concerning the addition of methyl or ethyl malonate or cyanoacetate to methyl or ethyl esters of β -vinylacrylic acid and its variously methylated derivatives, are quoted or newly recorded in Part IV (Bloom and Ingold, *J.*, 1931, 2765); they are here schematically summarised:

Vinylacrylic derivative	Parent	δ -Me	$\alpha\delta$ -DiMe	$\beta\delta$ -DiMe	$\gamma\delta$ -DiMe
Michael $\alpha\beta$ -adduct	0%	10%	2%	2%	50—70%

The exclusive δ -addition to vinylacrylic esters may be correlated with the conjugation between the ethenoid link and carboxyl group in one of the δ -addition products, and the absence of any adequately compensating hyperconjugation in the β -addition product. The δ -methyl group of the sorbic ester, $\text{CH}_3\text{:CH:CH:CH:CH}\cdot\text{CO}_2\text{R}$, stabilises the β -addition product, quite considerably it appears, owing, as one may presume, to the hyperconjugation of the δ -methyl group with the $\gamma\delta$ -double bond in this isomeride. The effect of the hyperconjugation of this methyl group is, however, largely compensated by the introduction, additionally, of an α - or β -methyl group, which becomes hyperconjugated with the double bond in the δ -addition product. An additional γ -methyl group reinforces the energy effect of the δ -methyl group (probably slightly, in spite of the superficial appearance of the figures, owing to the logarithmic relation between composition and energy), presumably because the main energy effect is that of the doubly hyperconjugated MeC:CMe system in the β -addition product (the recorded heats of hydrogenation of simple olefins support this inference).

The observations on Michael and related additions to the phenylated derivatives of β -vinylacrylic esters are also quoted or reported in Part IV (*loc. cit.*). The presence of a phenyl group in the δ -position (without a similar group in the α - or β -positions), as in cinnamylideneacetic esters, $C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CO_2R$, leads to practically exclusive β -addition. Clearly, this mode of reaction preserves the phenyl-to-vinyl conjugation, the large resonance energy (7 kilocal.) of which may be held responsible for the direction of the addition. Michael reactions pursue the same direction even with cinnamylidenemalonic esters, $C_6H_5 \cdot CH:CH \cdot CH:C(CO_2R)_2$, in which an extra α -carboxyl group is present to enhance the tendency to δ -additions. However, it was shown in Part VI (Duff and Ingold, *J.*, 1934, 87), by study of the further transformations of the adducts under the conditions of their formation, that δ -addition has an appreciable rate in this case, and that the δ -addition product can be produced if it can simultaneously be consumed, even though it has a smaller thermodynamic stability than the β -addition product.*

Farmer and Martin have examined the addition of methyl malonate to a hexatriene ester, $CH_3 \cdot CH:CH \cdot CH:CH \cdot CH:CH \cdot CO_2Me$ (*J.*, 1930, 960). Here the malonic ester residue might add to the β -, the δ -, or the ζ -positions of the triply unsaturated ester, and in the last two cases the product might appear in more than one prototropic form. The investigators found 67% of β -addition, and between 10% and 33% of ζ -addition, whilst δ -addition, though not excluded, was not detected. (Prototropic forms were not distinguished, the first step in the analysis of the addition product being the hydrogenation of its surviving double bonds.) Theoretically, we can feel sure that no δ -addition took place, since it would break up the butadienoid conjugation completely, whereas β -addition preserves, and ζ -addition can preserve, a butadiene system (resonance energy ~ 3.5 kilocal.) in the product. In the β -addition product there is hyperconjugation between the terminal methyl group and the butadiene system. In one prototropic form of the ζ -addition product there is conjugation between the butadiene system and the carbomethoxyl group, whilst in the one other form which contains a butadiene system there is not; it is, however, possible that the prototropic system does not come fully into equilibrium under the mild conditions employed to effect this addition.

(e) *Hydrogenation by Dissolving Metals.*—Burton and Ingold's theory of these reductions (Part II, *J.*, 1929, 2202) appears to retain its usefulness (cf. Kuhn and Deutsch, *Ber.*, 1932, 65, 817; Kuhn and Hoffer, *Ber.*, 1933, 66, 1263; Ingold and Rogers, *J.*, 1935, 717), but we take the present opportunity to modernise and simplify its application to the reduction of conjugated systems.

A metal is regarded as an electron gas enclosed in potential walls, through which electrons can escape, either directly to an adsorbed cation, or to a cation through an adsorbed, conducting organic molecule, which thereby becomes reduced. The organic molecule needs an electron-accepting group, COR, CO_2R , etc. (even aryl can so act, though with more difficulty), in order to create the positively polarised position required for an adsorption which will provide a way of escape for the metallic electrons. Carbonyl or carboxyl groups may have their electron-affinity increased, by their engaging in a pre-equilibrium with an adding proton, in order to produce a sufficient positive polarisation; and the presence of a covalently or electrostatically bound proton in the electron acceptor will in any event be required to hold the electrons transferred from the metal to the reducible system. Although desorption of the latter may take place after the reception of only one electron, as in pinacol formation, it occurs more normally when two electrons have been taken up, octets have been completed, and a negative charge has been acquired by the organic group. The components ($H^+ + 2e$) of a hydride ion (H^-) have now been added in this surface reaction, which is evidently to be classified as heterolytic. After desorption, the reduction is completed homogeneously † by the addition of a proton (H^+).

In the case of a butadiene system with an electron-accepting α -group, the positive polaris-

* Malachowski, Bilbel, and Bilinski-Tarosowicz (*Ber.*, 1936, 69, 1295) obtained a normal addition product (ethyl 1-benzylpropane-1:1:2:3-tetracarboxylate) from ethyl benzylmalonate and ethyl fumarate, whereas Rydon (*J.*, 1935, 420; cf. Ingold and Rydon, *J.*, 1935, 857) had obtained an abnormal product (ethyl 1-benzylpropane-1:2:3:3-tetracarboxylate), having a transferred carboxyl group, and Duff and Ingold (*loc. cit.*), before that, had obtained a product which was probably abnormal, although they had given it the normal formula. (They were interested only in its decarboxylated hydrolysis product, α -benzyltricarballic acid.) The first-named authors seem to be unaware that, by a series of reactions (Dieckmann ring-closure and alcoholysis) first elucidated by Holden and Lapworth (*J.*, 1931, 2370), and well supported subsequently, normal and abnormal Michael addition products are generally interconvertible under the experimental conditions of Michael reactions, and that, in particular, it is commonly possible to obtain a normal product in place of an abnormal one by a suitable adjustment of conditions.

† We regard this reaction as homogeneous for lack of more intimate knowledge, but it may in some cases occur very quickly after desorption.

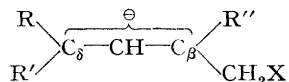
ation, and therefore the adsorption, will take place at the δ -end of the conjugated chain, for just the reason already given for the terminal initiation of the other types of addition reaction. At the desorption stage, the δ -position will be negatively charged. In some structures the charge may be held in this position by a second electron-absorbing group until combination with a proton supervenes. Thus we interpret the 1 : 4-reduction of $\alpha\delta$ -diphenylbutadiene, cinnamylideneacetic acid, and muconic acid, and, likewise, the 1 : 6-reduction of $\alpha\zeta$ -diphenylhexatriene, and so on. In the more general case the charge will become distributed in the desorbed mesomeric anion, so that (from butadiene compounds) 1 : 2- and 1 : 4-reduction products will be formed side by side.

In almost all cases the position taken up by the proton linked in the final stage of reaction will be kinetically, and not thermodynamically, controlled. If this were not so, butadiene-1 : 4-dicarboxylic (muconic) acid, for example, would not, by treatment with sodium amalgam, yield but-2-ene-1 : 4-dicarboxylic acid, but would give the more stable but-1-ene acid, into which the but-2-ene acid can in fact be converted by alkalis at higher temperatures than those which suffice for the reduction. This, indeed, is a case in which the equilibrium between the possible reduction products is comparatively easily set up : in most other cases, including those discussed below, the conditions of reduction will be milder by a still larger margin than those necessary to bring to equilibrium the three-carbon system involved in the final reaction-stage.

Burton and Ingold examined experimentally the proportions in which $\alpha\beta$ - and $\alpha\delta$ -dihydro-compounds were formed by reduction with amalgams from vinylacrylic acid, $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, and certain methylated derivatives, in some cases using acidic as well as alkaline solutions, *i.e.*, operating with the free acids as well as with their anions. The results of these authors' analyses of the dihydro-products are summarised in the following scheme :

Vinylacrylic derivative	$\alpha\beta$ -Dihydro-isomeride from			
	Parent	δ -Me	$\beta\delta$ -DiMe	$\beta\delta\delta$ -TriMe
Alkaline medium	0%	40%	28%	38%
Acidic ,,	18%	55%	—	—

The mesomeric anion concerned in the final reaction-stage in all these cases may be represented by the formula



where R, R', and R'' may be either H or Me, and CH_2X may be either $\text{CH}_2\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\cdot\text{CO}_2^-$. Burton and Ingold discussed the relative rates of proton combination at the β - and δ -positions on the hypothesis that the inductive effect of alkyl groups "repels" the negative charge to the more remote of the two positions. Now we realise that alkyl effects are hyperconjugative, rather than inductive, *i.e.*, that they have their origin in a quantal resonance, rather than in electrostatic forces. Hence we must put the theory on to the basis (which is equivalent in its results) that alkyl groups "attract" the double bond, *i.e.*, tend to fix it in the position permitting hyperconjugation. Here we may point out that, unlike aryl, carbonyl, or carboxyl groups, which could in principle conjugate either with the lone electrons of the anionic charge or with the π -electrons of the double bond, alkyl and substituted alkyl groups can hyperconjugate only with the double bond. The direction of the electron redistribution involved in

hyperconjugation is unambiguous, $\text{Alk}-\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowleft}{\text{C}}$, and hence we can at once write down the series ($\text{Alk} =$) $\text{CH}_2\cdot\text{CO}_2^- > \text{CH}_3 > \text{CH}_2\cdot\text{CO}_2\text{H} > \text{H}$ for the relative importance of the effect in the cases summarised in the above general formula. It is to be emphasised, however, that we are not here dealing with a fully formed double bond, as in an equilibrium problem, but only with the developing double bond present in each of the alternative transition states of the final proton union. Hyperconjugation in these states, however, will undoubtedly affect the relevant activation energies, for there is plenty of indirect evidence in the behaviour of pseudo-acids (this vol., p. 11) that the formation of a prototropic system from its ions is an activated process.

With these ideas in mind the qualitative relationships shown in the preceding figures can readily be understood. In the presence of only a single hyperconjugating group, $\text{CH}_2\cdot\text{CO}_2^-$, the most powerful of the above series, in the β -position, proton combination takes place nearly exclusively in the δ -position. With a weaker β -group, $\text{CH}_2\cdot\text{CO}_2\text{H}$, or with the same β -group, $\text{CH}_2\cdot\text{CO}_2^-$, partly compensated by a weaker δ -group, CH_3 , the want of balance is reduced but

not inverted. With the weaker β -group, $\text{CH}_2\cdot\text{CO}_2\text{H}$, over-compensated by the stronger δ -group, CH_3 , the unbalance is inverted. The effect of a δ -methyl group is seen to be partly undone by an added β -methyl group, and partly restored again by an added *extra* δ -methyl group.

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