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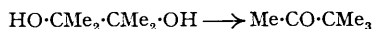
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*Old and New Ideas on Saturated Rearrangements.*

By C. K. INGOLD, D.Sc., F.R.I.C., F.R.S.

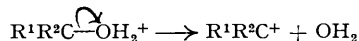
REARRANGEMENTS in saturated systems occur in reactions of various stoichiometries, for example, in substitutions, eliminations, and additions. Isomeric change can be regarded as a special case of substitution with rearrangement. Despite the stoichiometric differences, the rearrangements exhibit a close family resemblance. Their oldest history belongs to carbonyl-forming eliminations.

In 1859 Fittig discovered pinacol, and in 1860 he observed its conversion by sulphuric acid into a ketone, pinacolone (pinacolin) (*Annalen*, 1859, **110**, 17; 1860, **114**, 54). The striking feature of this change is the shifting of a methyl group from the carbon atom which is increasing its binding with oxygen, to the carbon atom which is losing its oxygen:



Many conversions of this type have since been realised. The original glycol need not be di-tertiary, but may at least be tertiary-secondary, tertiary-primary, or disecundary. And the shifting group need not be methyl, but may be any alkyl or aryl group.

Much work has been done on this reaction in order to determine what are called the relative migratory aptitudes of groups, though this phrase tends to mix up two questions which should be taken in order. The first is that of which hydroxyl will be lost, when the glycol  $\text{HO}\cdot\text{CR}^1\text{R}^2\cdot\text{CR}^3\text{R}^4\cdot\text{OH}$  is treated with acid; because that determines which of the two pairs of R's will furnish an R to replace it. This being settled, the second question has meaning, namely, which member of the relevant pair of R's will be so furnished. The answers have been known since 1929 (*Ann. Reports*, 1928, **25**, 133; cf. Shoppee, Thesis, London, 1929). The first is that acid-catalysed hydroxyl loss, with rearrangement, from  $\text{RR}'\overset{\text{I}}{\text{C}}\cdot\text{OH}$ , is facilitated by inductive and conjugative electron release from  $\text{RR}'$ , just as in ordinary unimolecular substitution or elimination, without rearrangement, from the conjugate acid of an alcohol:



The second answer is that, of a given pair of groups  $\text{R}^3\text{R}^4$ , that group will migrate best which can best provide electrons: in other words the migrating group behaves as an internal nucleophilic reagent towards an electron-demanding centre.

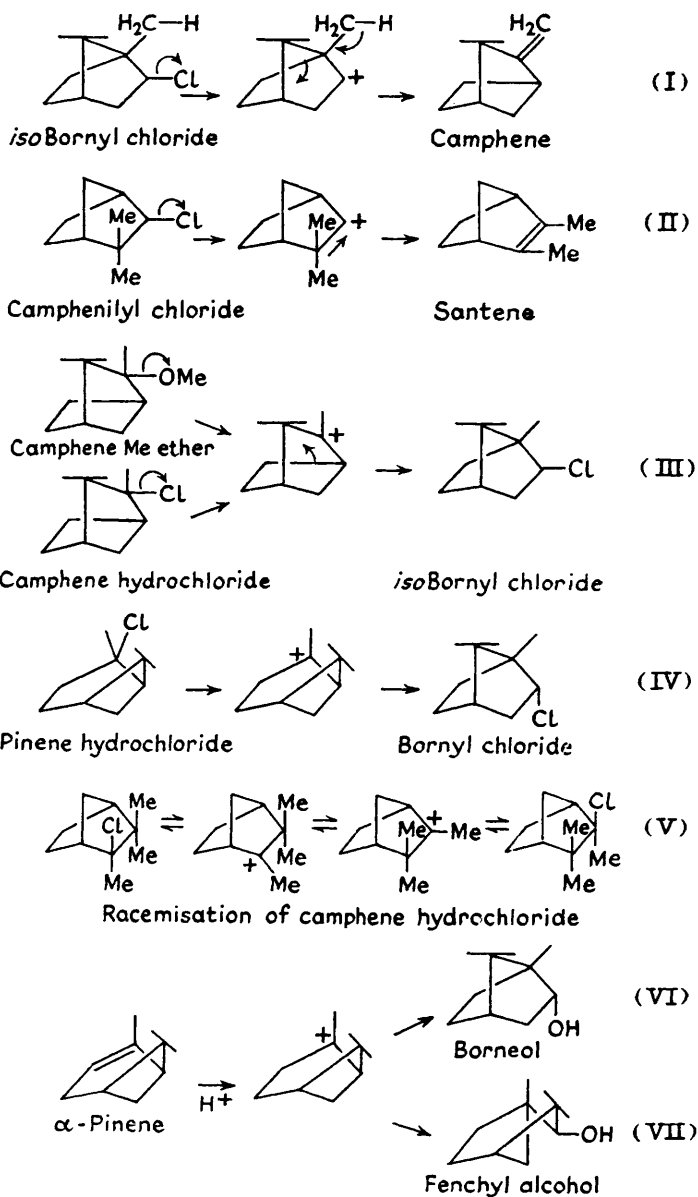
A number of rearrangements are known which are such obvious variants of the pinacol-pinacolone conversion that we can regard them as covered by our discussion of this change. They include the rearrangements of epoxides, the acyloin rearrangement, the aldehyde-ketone rearrangement, the benzil-benzilic acid conversion, the iodohydrin rearrangement, and pinacolic deamination. We shall not find it necessary to discuss them independently.

The other large group of rearrangements in saturated carbon systems belong to olefin-forming eliminations, and their reversal in the corresponding additions, and to the often concomitant nucleophilic substitutions: we call all these changes, independently of their stoichiometry, Wagner-Meerwein rearrangements.

They were discovered by Wagner in 1899, who recognised them as necessary for an interpretation of relations between different dicyclic terpenes (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 680; *Ber.*, 1899, **32**, 2302). Considering that in 1899 not a single dicyclic terpene had a firmly established structure, Wagner's combined deduction of the structures and of their interrelation through a previously undiscovered type of rearrangement must be counted a work of genius. Meerwein generalised Wagner's process, carried it outside the closed circle of bridged rings, and made it a phenomenon of organic chemistry, not only one of terpene chemistry (*Annalen*, 1910, **376**, 152; 1913, **396**, 200; 1914, **405**, 129; 1918, **417**, 255). Meerwein also made a major contribution, indeed the basic one, to the elucidation of the mechanism of the change, as we shall note later.

The following formulæ illustrate some cases, taken from the field of terpene chemistry. Stoichiometrically, some are olefin-forming eliminations (I and II), some nucleophilic sub-

stitutions (III, and the isomeric changes, or "symmetrical substitutions," IV and V), and some olefin additions (VI and VII). In spite of that, they all conform to a common pattern, if, following Meerwein's lead, we represent them as proceeding through a carbonium ion. Either a



ring-loop or a methyl substituent may move over from adjacent tertiary or quaternary carbon to the carbonium ionic centre.

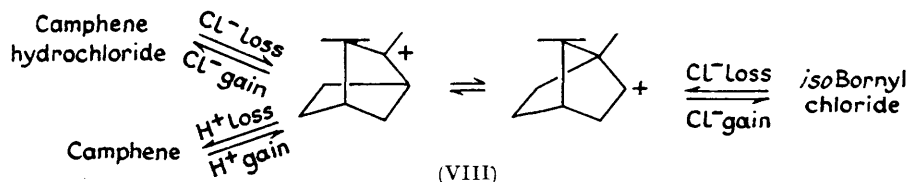
However, there are evident stereochemical restrictions on what does move over. For we cannot but notice that, in olefin-forming eliminations (I) and substitutions (III and IV), the initially detached substituent leaves carbon from the side opposite to that to which the ring-loop becomes bound; and likewise that, in substitutions (III and IV) and olefin additions (VI and VII), the finally entering substituent becomes bound to carbon on the side opposite that from which the ring-loop leaves.

When a methyl group shifts, as in santene formation (II), or in the interpretation (Simonsen and Owen, "The Terpenes," Vol. II, Cambridge Univ. Press, 1949, p. 290) of the racemisation of camphene hydrochloride (VI), and hence of camphene or of *isobornyl* chloride, the stereochemical rules may well be the same, though this cannot be deduced from the structures concerned in the absence of isotopic labelling.

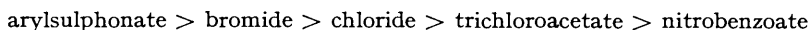
As before, we shall not separately consider obvious variants of the main process, but will take the Demjanow rearrangement, for example, to be included by implication in our discussion of Wagner–Meerwein changes.

The early theories of pinacol–pinacolone and related rearrangements need not long engage our attention. About 1880, Breuer and Zincke suggested epoxides (*Annalen*, 1879, **198**, 141), and Erlenmeyer cyclopropanes (*Ber.*, 1881, **14**, 322), as intermediates. But at that time little was known of the properties of either epoxides or cyclopropanes. In 1905, Tiffeneau advanced the hypothesis of free-radical intermediates (*Bull. Soc. chim.*, 1907, **1**, 1221). Again, at that date no one knew much about free radicals. As our knowledge grew of the types of structures postulated, all these theories were seen to be inadequate.

The year 1922 marks, with a paper by Meerwein and van Emster, the beginning of the modern theory of saturated rearrangements (*Ber.*, 1922, **55**, 2500). These authors had made a kinetic study of certain rearrangements, notably, the conversion of camphene hydrochloride into *isobornyl* chloride; and they built up a strong case for the view that these rearrangements depend on ionisation, the alteration of carbon framework occurring in the carbonium-ion stage (VIII):

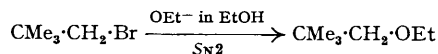


They offered two main reasons for this view. One was that the first-order conversion rates depended on solvent in a way which was clearly to do with ionising power, as could be checked by reference to the ionisation of triphenylmethyl chloride in the same solvents. The other reason was that those inorganic halides, such as  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ , and several others, which form additive ionic compounds with triphenylmethyl chloride, are powerful catalysts for rearrangement, while those, such as  $\text{SiCl}_4$ ,  $\text{PCl}_5$ , which do not unite with triphenylmethyl chloride, do not catalyse rearrangement. Later, Meerwein with other collaborators added a third reason, namely, that mobility increases with the stability of the detachable substituent, as an anion: among camphene esters, for example, the following rate series was established (*Annalen*, 1927, **453**, 16):



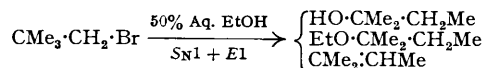
Later still, in 1929, I supplied a fourth reason, which was the point mentioned already, namely, that electron-supply to the atom from which, according to theory, the anion is required to separate, is indeed needed to facilitate the rearrangement. And so, by 1930, a very substantial body of evidence had been accumulated in favour of Meerwein's theory.

During the 1930's Whitmore extended our knowledge of the Wagner–Meerwein change in the acyclic series (*J. Amer. Chem. Soc.*, 1932, **54**, 3431; 1933, **55**, 4161; 1939, **61**, 1586). He found that *neopentyl* alcohol and its halides would undergo certain standard forms of nucleophilic substitution only with great reluctance; but that such substitutions, with accompanying eliminations, could easily be effected by certain special methods, for instance, by treatment of the halides with aqueous silver or mercuric salts; and that then the products are rearranged *tert.*-amyl compounds or *isoamylene*. In 1946 Dostrovsky and Hughes carried this demonstration to a conclusion [*J.*, 1946, 157 *et seq.* (6 papers)]. They showed kinetically that the substitutions that proceeded tardily were  $\text{S}_{\text{N}}2$  substitutions, and that the products were unrearranged, as in the following example:



They showed also that the ready nucleophilic substitutions or eliminations were unimolecular

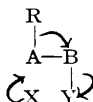
processes  $S_N1$ , or catalysed unimolecular processes, and that when this type of mechanism could be kinetically established, the products were rearranged, as indicated below :



This kinetic work at once linked up the study of rearrangements with that of unimolecular reactions of substitution and elimination in general, and thus brought to bear on the rearrangement problem the whole weight of our accumulated knowledge of the mechanism of unimolecular reactions. The subsequent study of saturated rearrangements derives its direction from this link-up.

First, however, there is a little more to be said about the work of the 1930's, and early 1940's. Notably, Whitmore pointed out that rearrangements are known, which are similar to the pinacol-pinacone and Wagner-Meerwein rearrangements, but involve nitrogen-containing systems, as in the Curtius, Hofmann, and Lossen rearrangements (*J. Amer. Chem. Soc.*, 1932, **54**, 3274). All these reactions can be regarded as dependent on the production of an electron-deficient atom, whether carbon or nitrogen.

Then, as to the stereochemistry of saturated rearrangements, a number of early results were available to convince us, as illustrated already, that we have configurational inversion at atom A from which migration starts, and also inversion at atom B on which migration ends, as indicated in the following expression :



This is written as for a substitution, but by the prior insertion of a bond AX, it can do duty for an elimination, and by making the B-Y bond initially double, it can serve for the case of addition. The older results, such as have been illustrated, applied primarily to Wagner-Meerwein changes; but it was shown in the later 1930's, particularly by Bartlett (*J. Amer. Chem. Soc.*, 1937, **59**, 820; 1938, **60**, 2416; 1940, **62**, 2927) and by Whitmore (*ibid.*, 1939, **61**, 1324), that similar conclusions hold for pinacol-pinacone rearrangements.

As to the configurational effect in the migrating group R, it has not even yet been directly proved for the pinacol-pinacone or Wagner-Meerwein changes, but it has been shown, particularly by Wallis (*J. Amer. Chem. Soc.*, 1926, **48**, 169; 1931, **53**, 2787; 1933, **55**, 1701; 1941, **63**, 1674) and by Kenyon (*J.*, 1939, 916; 1941, 263; 1946, 25), for the related Beckmann, Curtius, Hofmann, Lossen, Schmidt, and Wolff rearrangements, that at this point in the molecule configuration is preserved.

Since 1946 the objective of investigation has shifted from the space-relations to the time-relations between the component covalency changes. It is convenient for some purposes to regard the rearrangement as two substitutions, one at B and one at A, interconnected by the migration of R. We have to ask, first, whether the electron transfers at B are synchronous or not, that is,  $S_N2$ -like or  $S_N1$ -like, and, secondly, whether those at A are synchronous or not. We shall find that either question may have either answer, and that, consequently, a plurality of mechanism, similar to that encountered in more elementary reactions, applies also to these rearrangements.

We should note that the spatial relations between the covalency changes do not answer these questions, except in a permissive way. If substitution at B, for instance, were  $S_N2$ -like, then there would be inversion. But so there would if it were  $S_N1$ -like, provided that R begins to move over before Y has receded out of shielding range, say, about 5 Å. The stereochemical result shows only that R does begin to move over before Y has gone as far as that.

However, the energetically important question is whether R begins to move over before Y has receded to its transition-state distance, that is, by about 0.35 Å. If it does not, then the separation of Y will not be kinetically affected by the migration of R, and the substitution at B will be classed as step-wise, or  $S_N1$ -like. Its rate will be about the same as that of any unimolecular reaction in which the same type of heterolysing bond has the same immediate local surroundings in simple molecules. If the migration of R does begin before Y has receded to its transition-state distance, then the substitution will be  $S_N2$ -like. The reaction will now be "accelerated"; this means that we may find it going thousands of times faster than if the same heterolysing bond had the same local surroundings in simple non-rearranging molecules.

Our rate standards are quite definite to within structurally trivial factors, such as 2 or 3. In

unimolecular reactions we have no general complications due to steric hindrance, and therefore, in saturated systems, in which weak polar effects are largely localised, rate of heterolysis structurally depends essentially on the heterolysing bond and the atoms immediately next to it. Thus to within the limits mentioned, all tertiary alkyl chlorides are heterolysed at the same rate, as is illustrated by the following relative rates of solvolysis in 80% aqueous alcohol at 35°; and all tertiary iodides are also heterolysed at almost the same rate :

	Me·CMe <sub>2</sub> ·	Et·CMe <sub>2</sub> ·	Pr <sup>n</sup> ·CMe <sub>2</sub> ·	Bu <sup>n</sup> ·CMe <sub>2</sub> ·	n-C <sub>5</sub> H <sub>11</sub> ·CMe <sub>2</sub> ·
Chlorides .....	1.00	1.61	1.41	1.33	1.21
Iodides .....	1.00	1.85	1.77	1.75	1.53

So are tertiary alkylsulphonium salts, and likewise secondary alkyl bromides, primary alkyl bromides, and so on—always, be it noted, as long as the reactions remain unimolecular.

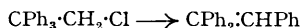
Against that background, let us notice some rates of rearranging reactions. Most of the examples I shall give are due to Prof. E. D. Hughes and his colleagues and pupils, who have been studying this subject since they published their linking-up papers of 1946. The simplest case is the solvolysis of *neopentyl* bromide to give *tert.*-amyl products (Dostrovsky and Hughes, *J.*, 1946, 164, 166, 171). As the following figures illustrate, the unimolecular rate is about the same as for other primary bromides, for instance, ethyl bromide :

Hydrolysis in wet H·CO<sub>2</sub>H at 95° { ethyl bromide,  $k_1 = 2.70 \times 10^{-6}$  sec.<sup>-1</sup>  
*neopentyl* bromide,  $k_1 = 1.53 \times 10^{-6}$  sec.<sup>-1</sup>

Evidently the migrating methyl group in the *neopentyl* group does not assist heterolysis of the halogen, even though the migration must occur before the halogen has passed out of shielding range, since no appreciable quantities of unrearranged solvolysis products accompany the rearranged products. Again, as the next set of figures exemplifies (Hughes *et al.*, *Nature*, 1950, 166, 679) the solvolysis of pinacolyl chloride, CMe<sub>2</sub>·CHMe·Cl, also to give exclusively rearranged products, goes at almost the same unimolecular rate as would apply to any simple secondary chloride, such as *isopropyl* chloride :

Solvolysis in 80% aq. EtOH at 80° { *isopropyl* chloride,  $k_1 \sim 5 \times 10^{-7}$  sec.<sup>-1</sup>  
 pinacolyl chloride,  $k_1 = 1.94 \times 10^{-7}$  sec.<sup>-1</sup>

Now let us notice some accelerated rearrangements. Hughes obtained one by replacing the three methyl groups of *neopentyl* chloride by three phenyl groups, to give 2 : 2 : 2-triphenylethyl chloride, which is solvolysed with exclusive rearrangement to give triphenylethylene :

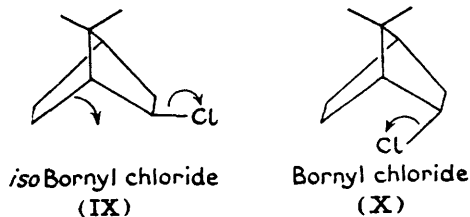


But this solvolysis in formic acid goes 60,000 times faster than that of *neopentyl* chloride, and therefore faster by factors of that order than those of simple non-rearranging primary chlorides (Charlton, Dostrovsky, and Hughes, *Nature*, 1951, 167, 986) :

Hydrolysis in wet H·CO<sub>2</sub>H at 95° { *neopentyl* chloride,  $k_1 \sim 4 \times 10^{-8}$  sec.<sup>-1</sup>  
 2 : 2 : 2-triphenylethyl chloride,  $k_1 = 2.3 \times 10^{-3}$  sec.<sup>-1</sup>

Here, the migrating phenyl group is evidently helping to detach the chlorine, thus acting in a synchronous, S<sub>N</sub>2-like manner. The resulting acceleration has been called a *synartetic* acceleration, for a reason which will be explained later.

Bornyl and *isobornyl* chloride provide an interesting comparison among secondary alkyl chlorides. The solvolysis of bornyl chloride is unaccelerated. Its rate is compared below with that for pinacolyl chloride, which we have already compared with the rate for *isopropyl*



chloride. The solvolysis rate of *isobornyl* chloride is about 100,000 times greater (Brown, Hughes, Ingold, and Smith, *Nature*, 1951, 168, 65) :

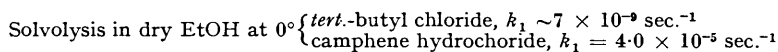
Solvolysis in 80% aq. EtOH at 80° { pinacolyl chloride,  $k_1 = 1.94 \times 10^{-7}$  sec.<sup>-1</sup>  
 bornyl chloride,  $k_1 = 1.5 \times 10^{-7}$  sec.<sup>-1</sup>  
*isobornyl* chloride,  $k_1 = 1.4 \times 10^{-2}$  sec.<sup>-1</sup>

The products from either isomer are camphene derivatives. The idea that the fast reaction owes its high rate to synartetic acceleration accords well with the stereochemical situation. For in the *isobornyl* compound the bond shift could be initiated before the chlorine had receded to the separation of the transition state of its ionisation, and therefore could have an accelerative effect on the rate (IX). But in *bornyl chloride*, no bond shift can commence until the chlorine has moved right out of the way, to well beyond the transition-state separation, and therefore the bond shift must come in too late to influence the rate (X).

In these examples we have the dual answer concerning the relative timing of covalency changes at atom B, on which migration ends. A similar duality could be illustrated for atom A, from which migration begins; but we can assume that to follow, without special illustration, from the known reversibility of Wagner–Meerwein rearrangements, A and B having interchangeable functions. When we put the two dualities together, we obtain at first, as the following Table shows, a four-fold classification, according to whether the three covalency changes are all separate in time, or whether the first two, or the second two, or all three, become synchronised. But, actually the fourth class cannot be illustrated; and the second and third are only forward and backward readings of the same reversible reaction. Thus we have two established kinetic types of rearrangement, which we may call the "normal-rate" type and the "accelerated" type.

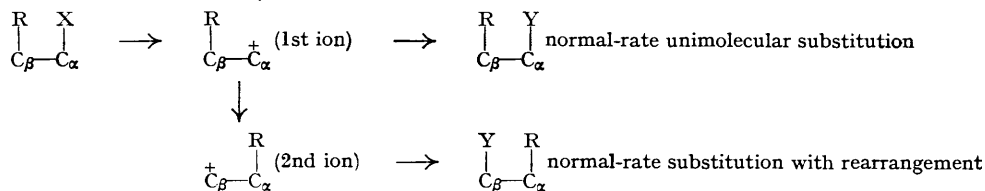
	Molecularity of "substitutions" at		Timing of the electron transfers	Example	Kinetic type
	B	A			
(1)	uni	uni	$a$ , then $b$ , then $c$	<i>neo</i> Pentyl $\rightarrow$ <i>tert.</i> -amyl	Normal
(2)	bi	uni	$a + b$ , then $c$	<i>iso</i> Bornyl $\rightarrow$ camphene	Accel.
(3)	uni	bi	$a$ , then $b + c$	Camphene $\rightarrow$ <i>isobornyl</i>	
(4)	bi	bi	$a + b + c$	(None established)	—

As I have remarked already, the whole of this contemporary investigation of rearrangements arises from its absorption into the study of unimolecular reactions; and we have, indeed, been taking as our rate standards the rates of non-rearranging unimolecular reactions. Therefore the result next to be mentioned seems, at first sight, very surprising. It is that even non-rearranging unimolecular reactions are known which are accelerated. This may happen when the structure is prone to rearrangement, even if the rearrangement does not actually occur in the reaction showing the rate increase. The most familiar example is the aqueous hydrolysis of camphene hydrochloride to camphene hydrate and camphene. There is no rearrangement; but the rate is too great to be measured, and is obviously much greater than for simple tertiary chlorides. The rate of the corresponding ethyl alcoholysis has been measured by Hughes and his colleagues, and has been found to be 6000 times greater than for *tert.*-butyl chloride (*idem, ibid.*):



We interpret this as a quantal phenomenon, somewhat analogous to optical refraction or polarisability, which for any molecular state depends on all the *other* states the molecule *could* get into, even though the molecule is not utilising those possibilities.

As a preliminary to a more careful consideration (*idem, ibid.*) of this, and of the other phenomena illustrated above, let us start by restating Meerwein's theory in its wider setting of unimolecular reactions, as is here done in terms of chemical formulæ:



The rate-controlling step is heterolysis of the bond  $\text{C}_\alpha\text{—X}$  to give a carbonium ion. As the possibility of rearrangement has to be taken into account, we may call the obvious structure of this ion that of the "1st" carbonium ion. If this takes up an anion, or loses a proton, we have a non-rearranging unimolecular reaction. As we shall show, it is a normal-rate non-rearranging reaction. However, it is possible that a carbon atom with its full octet of electrons may move over from an adjoining position to the charge centre of the "1st" ion, thus producing a "2nd"

carbonium ion. If this takes up an anion, or loses a proton, we have rearrangement. We shall show that this is a normal-rate rearrangement.

The same theory is expressed in curves in Fig. 1, provided that we fix attention on the broken line there shown. Energy is being plotted against a reaction co-ordinate. The first diagram might represent *tert.*-amyl bromide ionising to give the *tert.*-amyl cation, which then simply yields *tert.*-amyl products. The representative point enters the diagram from the left, and goes out the same way, because the left-hand barrier lies lower. The possible rearrangement does not occur, because the energy barrier for ionisation of the *neopentyl* system, shown on the right of the diagram, stands higher. The theoretical possibility of such a rearrangement does not affect the left-hand energy levels, that of the 1st ion, and that of the transition state of its formation; and so we observe a normal-rate unimolecular reaction without rearrangement. The broken-line curve in the second diagram might represent *neopentyl* bromide ionising to the *neopentyl* cation, which then goes into the *tert.*-amyl cation, and finally into *tert.*-amyl products. Here, the representative point passes through from left to right. However, the later steps do not affect the energy of the "1st" ion, nor that of the transition state of its formation; and thus the total reaction is a normal-rate process, although it involves rearrangement.

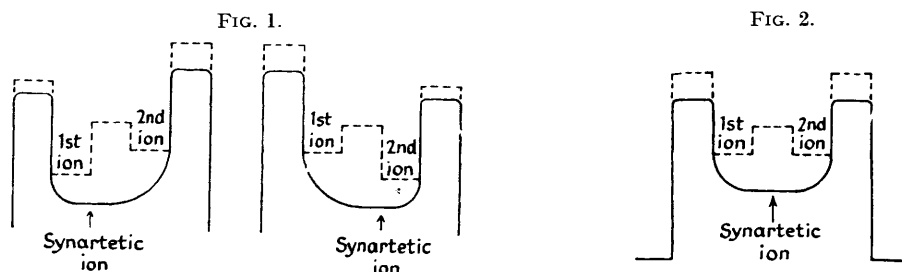
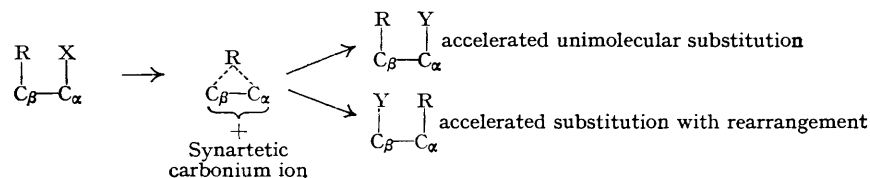


FIG. 1. Schematic representation of non-rearranging (left) and rearranging (right) unimolecular reactions, without (broken lines) and with (full lines) synartetic acceleration. Energy is being plotted against a reaction co-ordinate. The representative points enter from the left and leave mainly over whichever lateral energy-barrier lies lower.

FIG. 2. Schematic representation of symmetrical unimolecular substitutions, without (broken line) and with (full line) synartetic acceleration. Energy is plotted against a reaction co-ordinate. The representative points enter from the left, and leave equally by the left and by the right, so that there is 50% of rearrangement.

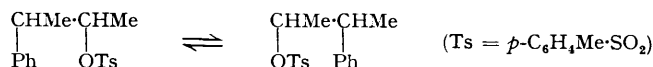
Now suppose that the barrier between 1st and 2nd ions is removed. The two ions will then cease to exist as individuals, their formulæ becoming no more than representations of brackets to the extra uncertainty of position now attaching to certain electrons. In our usual inaccurate language, we shall say that their resonance has produced a single ion more stable than either, a *synartetic ion*, as we may call it. The name means "to fasten together," because a single bond, that of the migratory group, is coupling the locations of an ionic charge split between the two possible centres. We have a more stable ion. Therefore we have more stable transition states of its formation, as shown by the full-line curves of Fig. 1. This follows because transition states, which themselves can be treated as resonance structures, reflect the stability changes of their factors and products. These full-line curves, then, having lowered energy barriers, illustrate accelerated reactions. The left-hand diagram might now represent the hydrolysis of camphene hydrochloride to camphene hydrate: it is accelerated, but goes without rearrangement. However, the acceleration is connected in an essential way with the presence of the molecular mechanism for accelerated rearrangement. The full-line curve in the right-hand diagram might represent the conversion of *isobornyl* chloride into camphene: it is accelerated, and goes with rearrangement.

We may now back-translate this extension of the Meerwein theory into terms of chemical formulæ:

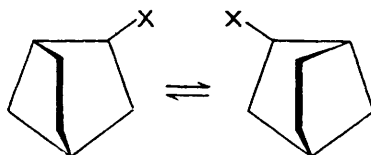


The rate-controlling stage is still the heterolysis of the bond  $C_{\alpha}-X$ ; but now the more stable synartetic ion is produced, and thus all unimolecular reactions are accelerated; whilst, according to the position in which the synartetic ion is attacked, the reactions will go without or with rearrangement. It will be clear why, no matter whether rearrangement occurs or not, we classify the accelerations as synartetic.

The symmetrical case, represented in Fig. 2, is realised when factor and rearrangement product are mirror-images, so that rearrangement can be followed by loss of optical activity. Cram has discovered a normal-rate case of this in the 1-methyl-2-phenylpropyl-toluenesulphonates (*J. Amer. Chem. Soc.*, 1949, **71**, 3863) :



Winstein and his collaborators have found a case involving a mild degree of acceleration in the *exo*-norbornyl benzenesulphonates whose rearrangement is like an *isobornyl*-ester-camphene-ester conversion, but with the three methyl groups removed, so that rearranged isomers become enantiomers (*ibid.*, 1952, **74**, 1127) :



Synartesis is concerned with the distribution over more than two atoms of  $\sigma$ -electrons only, and does not involve  $\pi$ -electrons. Mesomerism, on the contrary, is basically concerned with more-than-two-centre  $\pi$ -electrons. Furthermore, the pattern of valency and charge distribution in synartesis is quite different from that in mesomerism. Evidently the two phenomena are different enough to be treated as distinct.

The next question to which investigators will have to address themselves is obvious: When will synartetic acceleration occur, and when not? I think myself that the full answer will involve several conditions, including a suitable stereochemical arrangement and the absence of adequate stabilisation of an original cationic centre by mesomerism, that is, by ordinary conjugation or hyperconjugation. It appears, however, that, the necessary structural conditions being fulfilled, the carbonium carbon atom can do, what the isoelectronic neutral boron atom is certainly able to do, namely, split up  $\sigma$ -bonds. Such splitting seems always to take place when the only alternative would be to leave the fourth valency orbital unoccupied.