



Fig. 6. Plant grown for six months at 10° C. and 8-hr. day. After forming a terminal rosette the original shoot (left) was treated with gibberellic acid, which caused it to recommence elongating and at the same time stimulated a basal shoot to grow (right) although that shoot was not treated at any time. When treatment of the left-hand shoot ceased after a few weeks it formed a new terminal rosette but the new shoot continued to elongate without rosetting.

in that condition. Treatment with gibberellic acid, particularly after rosetting, also has the effect of stimulating the basal bud into growth, even though no acid is at any time applied to that bud or shoot, and there is a curious tendency for the new basal shoot to continue to elongate even after treatment with gibberellic acid has ceased and the original shoot has reverted to the rosetted condition (Fig. 6).

Heavier applications of gibberellic acid (for example, a single treatment with 200 µgm.) cause very rapid and abnormal elongation both of the rosetted apex and of the basal bud, which would not normally elongate until the following year, and the effects of such a single application persist for at least three months.

The importance of these results is that treatment with gibberellic acid changes the reaction of the plant to its environment, in this case causing a shoot to grow (that is, increase in length and leaf area) under weather conditions which would normally prevent it from elongating. By the use of appropriate dosages the growth made under the stimulus of gibberellic acid is quite normal and healthy.

Although the work on raspberry has little apparent application to general crop husbandry, it is not difficult to see the significance of these results. For various reasons such as risk of late frost or technical difficulties of cultivation, it is often necessary to delay the sowing or planting of crops, which make slow growth at first and may still be small when optimal growing conditions occur later in the season<sup>6</sup>. Earlier sowings may be useless in practice, since the young plants may fail to make appreciable growth under sub-optimal conditions of low temperatures or short days. However, if at this stage growth could be stimulated by chemical treatment under marginal weather conditions, but without causing the plant to initiate flower primordia, a larger plant might be produced by the beginning of the growing season, capable of taking full advantage of seasonal improvements in the weather. Crops might then make more total growth or might ripen earlier, or both.

The word 'marginal' is stressed. There is likely to be little profit in forcing plants to grow under dangerously sub-optimal conditions, and there might even be a risk of losing the crop altogether; but the careful control of plant behaviour in response to certain marginal weather conditions might offer a technique of considerable practical value in agriculture, enabling the farmer for the first time to break the grip of the weather on his crops. The work will continue in this Department with raspberries and a few other species, but the purpose of this article is to suggest that it might be worth while to make similar investigations on the major world crop species in centres where facilities exist for that type of work.

I am grateful to my colleague, Miss J. M. Cook, for the use of some unpublished results of her experimental contribution to this work.

<sup>1</sup> Went, F. W., "Experimental Control of Plant Growth" (Chron. Bot., 1957).

<sup>2</sup> Hudson, J. P., (Ed.), "Control of Plant Environment" (Butterworths Sci. Pub., 1957).

<sup>3</sup> Williams, I. H., and Hudson, J. P., *Nature*, **177**, 798 (1956); (and in the press).

<sup>4</sup> Williams, I. H., *Rep. Univ. Nottingham Sch. Agric.*, 1956, 44 (1957).

<sup>5</sup> Brian, P. W., *J. Roy. Soc. Arts.*, **106**, 425 (1958).

<sup>6</sup> Watson, D. J., in "The Growth of Leaves", ed. Milthorpe, F. L. (Butterworths Sci. Pub., 1956).

## STRUCTURE AND REACTIONS IN ORGANIC CHEMISTRY

### THE KEKULÉ SYMPOSIUM

A SYMPOSIUM on Theoretical Organic Chemistry was held in London during September 15–17 in celebration of the centenary of the discovery by Kekulé of the quadrivalency of carbon. Organized by the Chemical Society on behalf of the Organic Chemistry Section of the International Union of Pure and Applied Chemistry, the meetings were devoted to invited lectures and papers on chemical binding and structure, nucleophilic reactions, and electrophilic and homolytic reactions. The proceedings will be published in full.

It is probably true to say that no single paper has had so fundamental and far-reaching an influence on the development of organic chemistry as has Kekulé's paper of 1858 on "The Constitution and Metamor-

phosis of Chemical Compounds and the Chemical Nature of Carbon" (*Annalen der Chemie*, **106**, 129; 1858). It was in this paper that Kekulé clearly recognized that carbon is tetravalent and that carbon atoms can link together. These two concepts produced order out of chaos, led to the confirmation of the principle of homology, to the idea of closed rings and, in 1865, to the structure of benzene itself. Modern structural organic chemistry had begun, and the decades that followed saw the very rapid development of the subject which, with advancing years, included natural products and synthetic compounds of greater and greater complexity within its understanding. It was fitting, too, that this symposium should be held in London, because in 1854 Kekulé

was appointed as private assistant to J. Stenhouse at St. Bartholomew's Hospital, and it was while traveling on the upper deck of a Clapham omnibus on the return journey from a visit to Hugo Müller at Islington that he first conceived the basis of his now famous *Strukturtheorie*.

The symposium was formally opened by Prof. H. J. Emeléus (Cambridge), the president of the Chemical Society. Each of the three days opened with a lecture, which was followed by the reading of five papers. Sir Christopher Ingold (London), Prof. W. Doering (Yale) and Prof. R. Huisgen (Munich) acted as chairmen.

The symposium opened with a lecture by Prof. L. Pauling (Pasadena) on the nature of the double bond and of conjugated and aromatic molecules. He pointed out that, although the nature of the single bond is now well understood, there still remains some doubt about the best description of multiple bonds and of the structures of molecules in which these bonds are considered to play a part. Of the two ways of describing the double bond—first, as composed of a  $\sigma$ - and a  $\pi$ -bond, and secondly, as composed of two equivalent 'bent bonds', the second was preferred. "Bent bonds", it was maintained, "are best". The two descriptions are equivalent in the approximation in which the bond orbitals are *sp*-hybrids, but the inclusion of contributions from *d*, *f*, etc., orbitals to the bond orbitals results in concentration of the orbitals in the direction of the bond, and causes the two descriptions to differ significantly. In these circumstances, the 'bent bond' description was shown to afford superior interpretations of the observed magnitude of potential barriers to rotation about certain single bonds adjacent to multiple bonds, of the ratios between single, double and triple bond-lengths, and of observed bond-angles. Some implications of the 'bent bond' concept in considerations of the structure of aromatic compounds were also discussed.

A comparison of the results of the resonance and molecular-orbital theories when applied to the ground states of some  $\pi$ -electron systems was given by Prof. H. C. Longuet-Higgins (Cambridge). It was shown that the molecular-orbital theory is to be preferred in the treatment of molecules such as *cyclobutadiene* and *diphenylene*, containing unsaturated rings in which the number of  $\pi$ -electrons is not of the form  $(4n + 2)$ . The use of localization energies for predicting the reactivities of molecules in both heterolytic and homolytic reactions was also illustrated. Further work on the theory of aromatic character was described by Prof. D. P. Craig (London), in which the possibilities of  $\pi$ -electron delocalization of orbitals other than  $p\pi$ , such as  $d\pi$  and  $f\pi$ , were considered. In this wider framework aromaticity can be of two distinct kinds. Apart from the normal, or 'homomorphic' aromaticity, which is characterized by the prime role of the aromatic sextet, a second kind, called 'heteromorphic' aromaticity, is expected to occur in cyclic systems of alternating  $p\pi$ - and  $d\pi$ -orbitals, and should show no special preference for a sextet over an octet. Some features of the six- and eight-membered cyclic phosphonitrilic halides are compatible with delocalization of this type, and there are indications of the wider occurrence of this kind of aromaticity. The problems involved in the synthesis of new structural types possessing aromatic character were discussed by Prof. W. Doering (Yale). The structures discussed included the tropylium ion

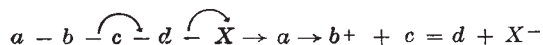
$C_7H_7^+$ , and its relatives, troponone and tropolone. Among neutral molecules, in the five-membered series fulvene,  $C_6H_6$ , has recently been obtained, and also probably fulvalene,  $C_{10}H_8$ , by an arduous removal of four hydrogen atoms from two molecules of *cyclopentadiene*. In the seven-membered series heptafulvene,  $C_8H_8$ , has been obtained in solution as an unstable, deep-red compound, and heptafulvalene,  $C_{14}H_{12}$ , has been obtained as a violet-red crystalline substance.

Attempts to provide quantitative experimental results to support quantum-mechanical calculations on conjugated systems by Kistiakowsky's classic method of measurement of heats of hydrogenation were described by Prof. R. B. Turner (Houston). In the more recent experiments described, it has been possible to apply corrections for steric strain energies to the measured total stabilization energies. Such corrections were shown in some instances to be large and important. In the last paper of the first day, Prof. C. A. Coulson (Oxford) discussed the influence of steric deformation and consequent departures from exact planarity on the  $\pi$ -electron structure of conjugated and aromatic molecules. The several distinct situations which can arise, namely, rotation about a formally single bond, as in diphenyl, large polynuclear over-crowded hydrocarbons like dibenzophenanthrene, where the strain is distributed over the whole molecule, phenanthrene-type distortions in which hydrogen atoms are displaced out of the plane, and buckled rings such as hexachlorobenzene, were considered separately.

The second day of the symposium was opened by Sir Christopher Ingold (London), who delivered a lecture on "Nucleophilic Octahedral Substitution". The displacement of the ligand X as an anion from various cobaltic ions of the form  $(Co en_2AX)^+$  is typical of this class of reaction, in which the regular space-figure involved is an octahedron. The kinetic characteristics of these reactions point to the dominance of two mechanisms, analogous to the known organic-chemical mechanisms  $S_N1$  and  $S_N2$ . The analogy extends fairly closely to the effects of substituent groups and of the nucleophilic capacity of the reagent on reactions by both mechanisms. The interpretation of the stereochemical results of these substitution reactions is complicated by the circumstance that the geometrical correlation between experimental result and molecular cause is less clear-cut in octahedral than in tetrahedral substitution. It appears that neither  $S_N1$ - nor  $S_N2$ -type octahedral substitutions by anions are stereochemically specific, although the latter show evidence of orientation, by the preserved ligands, caused principally by conjugative electron-displacement. However, octahedral substitutions of chloride ion by neutral water appear to proceed uniformly without stereochemical change. The theoretical implications of these findings and, in particular, of the differences between the neutral and anionic reagents, were discussed in detail.

Prof. J. D. Roberts (Pasadena) discussed the results of a kinetic investigation into the hydrolysis of diaryliodonium salts to phenols and aryl iodides. The reaction was studied under conditions likely to give rise to an  $S_N1$  mechanism, since under these conditions phenyl cations might be expected to be produced. However, the rather unexpected results which were obtained on the effects of substituent groups on the distribution of products, and the catalytic effects of oxygen, acids and copper salts

were taken as an indication that the complete reaction, which can be described as a nucleophilic substitution, involves the intermediate formation of solvent-caged free radicals. Recent research on the phenomena of fragmentation in solvolytic reactions was described by Prof. C. A. Grob (Basle). The heterolysis of a bond to an electron-acquiring group  $X$  in a system  $a-b-c-d-X$  may lead to the heterolysis of the bond between  $b$  and  $c$ , resulting in fragmentation ( $\beta$ -cleavage) of the molecule, as well as to the well-understood processes of substitution, elimination and rearrangement:



This can occur if  $a$  is an electron-donating group, and is particularly prevalent in  $\gamma$ -amino-halides, where  $a$  is  $-NR_2$ . Two unimolecular mechanisms for the fragmentation have been found to be operative, namely, a one-step process in which ionization of  $X$  and cleavage of the  $C_\beta-C_\gamma$  bond are synchronous, and a two-step mechanism in which the rate-determining ionization is followed by a faster product-determining step, which can lead to fragmentation or to other processes.

A review of recent progress in conformational analysis was given by Prof. D. H. R. Barton (London). The subjects discussed included the rearrangement of diaxial products of addition reactions to the cyclohexene system to the corresponding diequatorial isomers, which was illustrated by new rearrangement reactions of halohydrin esters. After a review, in conformational terms, of the behaviour of carbanions, Prof. Barton concluded his paper with a discussion of long-range group effects in large saturated molecules, such as steroid and other systems. It was concluded that these effects are transmitted by the successive distortion of valence angles. The effect is referred to as 'conformational transmission'. The  $S_N2$  mechanism of substitution at aromatic and other unsaturated centres was discussed in a paper by Dr. J. F. Bunnett (Providence). It was shown that in contrast to the synchronous  $S_N2$  mechanism of substitution at a saturated carbon atom, the  $S_N2$  mechanism in these examples involves the formation of metastable intermediate complexes. Often the bond to the incoming group is completed before the bond to the outgoing group starts to be broken. It is possible that the strictly synchronous  $S_N2$  mechanism is unique for displacements at saturated carbon. The role of 'benzyne' intermediates in rearrangements observed during nucleophilic aromatic substitutions with alkali amides or organolithium compounds was reviewed by Prof. R. Huisgen (Munich). Recent investigations were described which establish the mechanism more firmly and resolve some of the discrepancies attendant upon it.

Prof. M. J. S. Dewar (London) opened the last day of the symposium with a lecture on "Rearrangements in Aromatic Compounds". These rearrangements were classified and their possible mechanisms, including the intramolecular mechanism involving the formation of  $\pi$ -complexes, were discussed. New experimental work on the rearrangements of  $N$ -bromoacylanilide derivatives, and the acid-catalysed rearrangements of alkyl aryl ethers, was described. Both these rearrangements appear to be intermolecular. The mechanism of the benzidine and related rearrangements was discussed in the light of known experimental data, and the intramolecular

mechanism previously suggested by Prof. Dewar was shown to be not inconsistent with the recently discovered dependence of the rate of rearrangement on the square of the concentration of the acid catalyst.

Researches on the mechanism of nitration were reviewed by Prof. E. D. Hughes (London). Although the mechanism of nitration via the nitronium ion is very common, the paper included a discussion of nitration via nitrosation, and C-nitration via N-nitration and rearrangement. Work on O-nitration, which also proceeds via the nitronium ion, was discussed. Some recent studies of reactivity and orientation in aromatic halogen substitution reactions were described by Dr. P. B. D. de la Mare (London). Halogenation can take place either directly, by the molecular reagent, or with the intermediate formation of chlorine or bromine cations, or their hydrated forms. The conclusion that the inductive effects of substituent groups are less important in determining orientation in substitution by molecular than by charged species was reached from a consideration of recent work on halogenation, and was discussed in terms of the transition states for the two modes of substitution.

Recent evidence for the operation of quasi-heterolytic mechanisms for reactions in the gas phase was presented by Dr. A. Maccoll (London). The reactions considered, for which such mechanisms appear to be correct, were the unimolecular dehydrohalogenation of alkyl halides and olefin elimination from esters. The first group shows close similarities to the  $S_N1$  and  $E1$ , and the second to the  $E2$ , mechanisms for reactions in solution. The possibility of acid catalysis in the gas phase was discussed with reference to the elimination of olefins from alcohols catalysed by hydrogen halides. The remaining two papers dealt with homolytic reactions. Prof. D. H. Hey (London) described recent work on reactions of aroyl peroxides with naphthalene. The formation of aryl naphthalenes, naphthyl esters and dinaphthyls, and the proportions in which the various isomers of these substances were formed, were rationalized in terms of the various substitution and hydrogen-abstraction reactions which may occur with radicals of different polar and steric requirements. Recent measurements of the methyl (alkyl) affinities of various aromatic compounds and olefins were presented and discussed by Prof. M. Szwarc (Syracuse). The relationship between the experimental results and theoretical calculations of localization energies was shown to be consistent with a model of the transition state for attack by alkyl radicals in which the repulsion between the radical and the molecule and the attraction between the same radical and the 'residual' molecule (that is, a hypothetical molecule in which an electron is localized on one of the carbon centres) are balanced.

On the evening of September 15 those attending the symposium were invited by the University of London to a reception by the Vice-Chancellor (Dr. C. F. Harris) at the Senate House. On the following evening the Kekulé Symposium dinner was held at the Connaught Rooms, at which the speakers were Prof. H. J. Emeléus (president of the Chemical Society), Prof. P. E. Verkade (president of the Section of Organic Chemistry of the International Union of Pure and Applied Chemistry) and Prof. R. Huisgen.

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