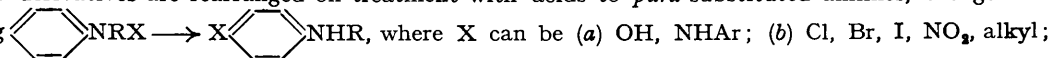


81. The Mechanism of Benzidine-type Rearrangements, and the Rôle of π -Electrons in Organic Chemistry.

By M. J. S. DEWAR.

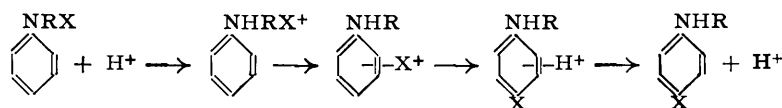
Recently (Dewar, *Nature*, in the press) a new mechanism for the benzidine rearrangement was proposed and its possible application to other rearrangements mentioned. A general theory is now presented which provides a large number of related rearrangements with a common and stereochemically possible background, and accounts for the reactions of olefins in a novel manner. The theory is based on the formal analogy between atomic and molecular orbitals and on the idea that π -electrons may be capable of forming dative bonds.

MANY aniline derivatives are rearranged on treatment with acids to *para*-substituted anilines, the general reaction being  where X can be (a) OH, NHAr; (b) Cl, Br, I, NO₂, alkyl; (c) NH₂, acyl, SO₃H; (d) Ar·N:N. The rearrangements of group (a) appear to be entirely intramolecular (Ingold *et al.*, *J.*, 1927, 1245; 1933, 984). Those of group (b) are at any rate partly intramolecular (cf. Orton *et al.*, *Brit. Assoc. Reports*, 1912, 117; *J.*, 1929, 915). Those of group (c) have not been investigated, and the rearrangements of diazoamino-compounds probably involve fission and resynthesis.

Electronic theories of these rearrangements have been published by Robinson (*J.*, 1941, 220) and by Hughes and Ingold (*ibid.*, p. 608). Both, however, involve serious stereochemical difficulties; in the transition states very long bonds and considerable distortion of bond angles would be required.

It is generally accepted that in these cases the migrating group migrates as a cation; it has not been remarked that in general the cation is derived from a stable anion by loss of two electrons. Now such an electron-deficient cation should be able to interact with the π -electrons of an aromatic system, exchange forces holding the two together. These exchange forces will constitute a definite chemical bond, differing from an ordinary bond only in that it links whole groups and not a pair of atoms. Otherwise it will be formally analogous to the bond in the helium molecule-ion, He₂⁺, where again a positive charge makes possible linkage between two otherwise saturated entities.

The positive ion will be able to move about over the π -electron layer of the aromatic system until it eventually displaces a hydrogen atom by cationoid attack. The exclusive *para*-orientation is to be expected by analogy with the *para*-diazo-coupling of aniline derivatives. The acid catalysis of these rearrangements is easy to understand on this basis; the general mechanism may be written:



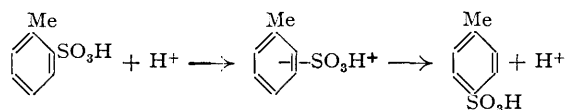
A somewhat different symbol for the intermediate " π -complex" has been used here; it seems more convenient than that in the original paper. In the formation of the π -complex the cation X⁺ is, of course, never detached; the nitrogen atom itself forms part of the extended aromatic system, and therefore the bonding of the migrating group can undergo transition to a π -bond before it has left the vicinity of the nitrogen atom. In the π -complex the positive charge will naturally be shared with the ring, since the positive ion is held by electron-exchange.

The stability of the complex will vary inversely with the stability of the positive ion. The ions OH⁺ and

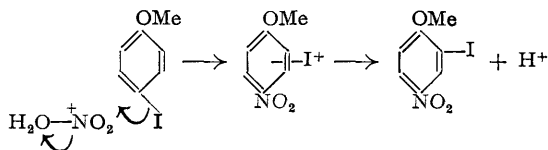
PhNH^+ must be very unstable; therefore the π -complexes formed by them are very stable and no migration to foreign nuclei has been detected in the semidine or phenylhydroxylamine rearrangements. On the other hand, the benzenediazonium cation is quite stable; it has therefore very little tendency to form a π -complex and so diazoaminobenzene rearranges by fission and coupling.

Intermediate stability would be expected for the ions in group (b); it is in just these rearrangements that the evidence of mechanism is most conflicting. The migrating groups can be transferred to other nuclei under suitable conditions and the rearrangements often occur partly by intermolecular processes. Nevertheless, Orton and his collaborators (*loc. cit.*), after a detailed investigation, concluded that the *N*-nitroaniline rearrangement is at least partly intramolecular and the same seems certainly true of the *N*-haloacetanilide rearrangements in aprotic solvents (Bell *et al.*, *Proc. Roy. Soc.*, 1934, A, 143, 377; 1935, A, 151, 211; *J.*, 1936, 1154, 1520; 1939, 1774). However, since the π -complexes in these cases are less stable, they should act as cationoid reagents and under suitable conditions substitute other molecules. This explanation of the migration of groups to foreign molecules seems far more attractive than any based on the occurrence of free cations in solution, as suggested, for example, by Israel, Tuck, and Soper (*J.*, 1945, 547).

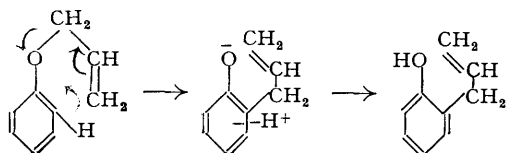
A number of other rearrangements probably involve similar intermediates. The interconversion of *o*- and *p*-toluenesulphonic acids in hot sulphuric acid was shown by Holleman and Caland (*Ber.*, 1911, 44, 2519) to be intramolecular; it can be formulated as



It is interesting that *m*-toluenesulphonic acid does not rearrange under these conditions; an *ortho*- or *para*-methyl group is required to activate the carbon bearing the sulphonic acid residue to cationoid attack. The Jacobsen rearrangement (cf. Smith, "Organic Reactions," Vol. 1, p. 370) has probably an exactly similar mechanism, an alkyl group or halogen migrating; here, transfer of the migrating group to another molecule has been observed. Another rearrangement of the same type has been reported in the nitration of *p*-iodoanisole (Reverdin, *Ber.*, 1896, 29, 1000); this may involve the mechanism

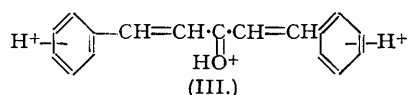
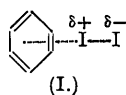


The *para* Claisen rearrangement and the catalysed rearrangements of alkyl aryl ethers may involve π -complex intermediates; the *ortho* Claisen rearrangement may also involve one, of different type. Since it is unlikely that free protons could be liberated in the absence of a base, the rearrangement may involve the following process:



In the representative rearrangements discussed above, π -complexes occur only as short-lived intermediates. Some evidence suggests, however, that they may be capable of stability of a much higher order.

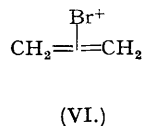
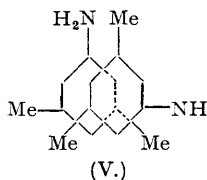
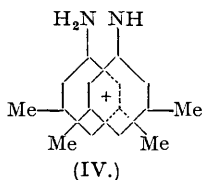
(1) Solutions of iodine in benzene have abnormal colour and dipole moments. These puzzling phenomena are at once explained if in them a π -complex is partly formed. It is not suggested that ionisation is complete, but that the product of interaction may be written as (I).



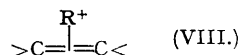
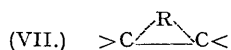
(2) Although anhydrous hydrogen fluoride does not dissolve paraffins and polymerises olefins, it dissolves aromatic hydrocarbons to give coloured solutions (Klatt, *Z. anorg. Chem.*, 1937, 234, 189), probably containing the hydrocarbon as cation (only bases and salts dissolve in anhydrous hydrogen fluoride). This cation can readily be formulated as a π -complex (II). Further investigation of these solutions would be of great interest.

(3) Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) have found that dibenzylideneacetone and cinnamylideneacetophenone give four-fold depression of freezing point in concentrated sulphuric acid; each molecule of ketone must therefore add three protons; this is readily understood if the products are π -complexes, *e.g.*, (III).

The rearrangements of hydrazobenzene derivatives are somewhat more involved since two benzene rings participate in the intermediate complex. The general course of the reaction was considered in the earlier paper and need not be recapitulated. It seems more likely, however, that the π -complex is formed by transformation of the N-N bond into a π -bond, the rearrangement thus falling into line with the others already mentioned. It is interesting that in the rearrangement of 3 : 5 : 3' : 5'-tetramethylhydrazobenzene an unusually large amount of diphenylene is formed (Carlin, *J. Amer. Chem. Soc.*, 1945, **67**, 928). In the configuration of the π -complex (IV) leading to the benzidine, both pairs of methyls are opposed and should sterically hinder each other; in the configuration (V) leading to the diphenylene only one pair of methyls is opposed.

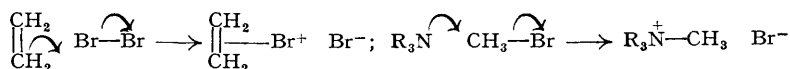


The formation of π -complexes should not be limited to aromatic systems, since olefins also possess π -electrons. A number of three-membered rings, postulated as reaction intermediates, are probably examples of π -complexes; thus in the addition of bromine to a double bond the cyclic intermediate is probably (VI). The pinacol-pinacolin and related rearrangements can also with advantage be interpreted with π -complex intermediates. According to the older ideas, the migrating group is, in the transition state, attached simultaneously to two atoms by partial bonds, the transition state being represented by (VII). The behaviour of *neopentyl* halides on hydrolysis (*cf.* Hughes, *Trans. Faraday Soc.*, 1941, **37**, 620) shows clearly, however, that in replacement on a carbon atom the partial bonds in the transition state must be linear, a condition not satisfied by (VII). The intermediate is better represented as a π -complex (VIII), in which the migrating group retains its normal valency and stereochemistry. Since the replacement of a normal bond by a π -bond may involve very little energy, no bond-stretching being necessary, the ease of these rearrangements, and particularly of rearrangements of aliphatic cations, is readily understood.



In the molecular orbital method of quantum-mechanical approximation, molecular orbitals do not differ essentially from atomic orbitals. The present theory suggests that if this be so, then the electron-pair occupying a molecular orbital should be available for dative-bond formation in the same way as is an unshared electron-pair on a single atom. The main requirement for such a molecular dative bond will be that the molecular orbital should overlap efficiently with the vacant orbital on the acceptor atom or group. For steric reasons σ -orbitals must be very inefficient in this sense, and therefore such molecular bonding can take place only with π -electrons, which are well adapted sterically for the purpose.

It has been difficult to explain in classical electronic theory why simple olefins should function so exclusively as anionoid reagents; cationoid reactivity, $X^- \text{CH}_2=\text{CH}_2$, would be expected to occur with almost equal facility, and is in fact commonly observed in conjugated systems. According to the present theory, the anionoid reactivity of simple olefins is due to a different process. The π -electron pair of ethylene, like the unshared pair in trivalent nitrogen, is available for dative-bond formation, and the reactions



are strictly analogous. In conjugated polyenes the ordinary electromeric processes may assume greater importance.

It may be added in conclusion that Pitzer (*J. Amer. Chem. Soc.*, 1945, **67**, 1126) has been led by somewhat different theoretical considerations to postulate a similar type of bonding in the hydroborons and salt-olefin complexes.