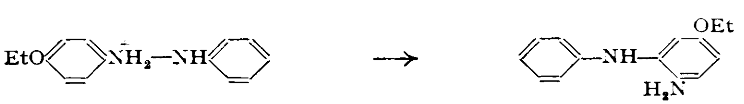
419. *The Stereochemistry of the Semidine Transformations.*

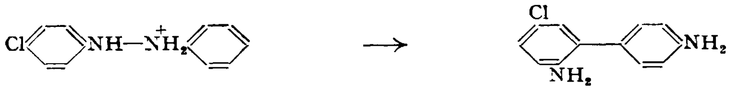
By D. Ll. Hammick and D. C. Munro.

By postulating activated states similar to those put forward previously (Hammick and Mason, *J.*, 1946, 638) to explain the stereochemistry of the benzidine transformation, it is possible to show that during the conversion of hydrazobenzenes into either semidines or diphenylines, the reacting centres can be brought to " ionic-bond " length (*ca.* 2·5 A.) before rupture of the N—N link.

It is shown that for the *p*-semidine transformation the nearest approach is 4·9 A.; as, however, the direction of interchange of fragments during *p*-semidine transformation is opposite to that which takes place during the *o*-semidine change, it is concluded that the two changes are possibly not analogous. This view is supported by the fact that (i) all the recorded cases of the *p*-semidine transformation are brought about indirectly by the reduction of certain azo-compounds by using stannous chloride, (ii) reduction of such azo-compounds in the absence of metal ions yields no *p*-semidine but good yields of *o*-semidine.

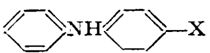
The *o*-semidine transformation of suitably substituted aromatic hydrazo-compounds is catalysed by all acids of sufficient strength. It is therefore reasonable to conclude that the transformation is, like the benzidine transformation (Hammick and Mason, *J.*, 1946, 638), a reaction of protonated hydrazines. The attachment of a single proton will be mainly to the more basic of the two imino-groups in the hydrazobenzene molecule, and it is possible to decide which is the more basic from the relative basicities of the corresponding substituted anilines (" fission bases "). It is found that with *para*-substituted hydrazobenzenes in which the *para*-substituted ring corresponds to the more basic aniline, semidines are formed. On the other hand, compounds, such as *p*-chloro- and *p*-bromo-hydrazobenzene, in which the *para*-substituted " fission base " is the less basic of the two give diphenylines. Thus :





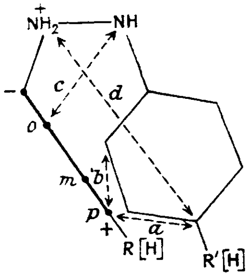
[The relevant basic constants are: *p*-phenetidine, $17{\cdot}9 \times 10^{-10}$; aniline, $3{\cdot}82 \times 10^{-10}$; *p*-chloroaniline, $0{\cdot}843 \times 10^{-10}$.]

The alternative *o*-semidine (shown inset) is apparently never formed (Jacobson, *Annalen*, 1922, **428**, 90—99, 106, 117).



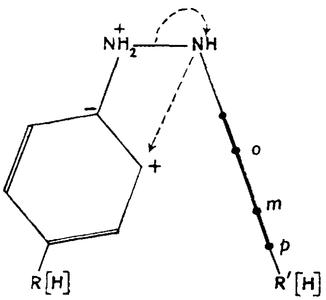
The intramolecular nature of the benzidine transformation of hydrazo-compounds must be regarded as established (Ingold and Kidd, *J.*, 1933, 984) and though there is no direct evidence in the case of the *o*-semidine transformation, the similarity between the conditions and results of the two processes makes it not unreasonable to suppose that both are intramolecular. The stereochemical implications of a continuous transition process in the case of the benzidine transformation have been discussed (Hammick and Mason, *loc. cit.*) in terms of the known bond lengths and interatomic distances. It was shown that in the various hybridised, semi-classical structures that can be written for the initial phase of the activated molecules undergoing the transformation, the *p*–*p*′ (and *p*–*o*′) positions come to within normal covalent bonding distances. The most significant of these structures is shown in Fig. 1.

FIG. 1.



(*a*) *Benzidine* 1·74 A.; (*b*) *diphenyline* 1·29 A.; (*c*) o-*semidine* 2·46 A. (*the value for the* o-*semidine change, is with the rings arranged as in Fig.* 2); (*d*) p-*semidine* 4·93 A.

FIG. 2.



It will be seen in Fig. 1 that the critical distance *c* for an *o*-semidine transformation is 2·46 A.,* which is of the order of an " ionic bond " in say a crystal of sodium chloride. Even if, therefore, during the passage through the transition state shown in Fig. 2, the positive charge at *o* in the left part is at a distance of about 2·5 A. from the negative nitrogen atom in the right part, the two fragments will be prevented from separating by the strength of an ionic bond.

The failure, in general, of hydrazo-compounds to give *o*-semidines when benzidines are possible, can be related to the greater energy required to set up the *o*-quinonoid resonance structures involved in the transition over that required for *p*-quinonoid structures. This mechanism is essentially a modification of that due to Robinson (*J.*, 1941, 220), and attempts to fulfil the stereochemical requirements of a continuous process, the aspect with which we are primarily concerned. Dewar (" Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, pp. 233 *et seq.*) puts forward a mechanism which depends on the assumption of the primary dissociation of a hydrazo-molecule, such as hydrazobenzene, into aniline and a positive ion, $C_6H_5{\cdot}NH^+$. Cationoid attack by this ion on the aniline by the $-NH^+$ or by the *o*- and *p*-positive centres derived from it, lead to the known semidines, diphenylines, and benzidine derivatives. Separation of the cation and the aniline is prevented by π bonding. It is not immediately apparent how the π-bond formulation, in terms of a bond of indeterminate length and unknown strength, can provide a satisfactory way out of the stereochemical difficulties.

The relation of the *p*- to the *o*-semidine transformation presents problems which have not always been fully appreciated, although they are outlined by Jacobson (*loc. cit.*, pp. 106—117). In general, *p*- and *o*-semidine formation occur together, and without diphenyline formation; this suggests, but does not prove, the primary attachment of a proton to the same imino-group

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* The values used for bond lengths are those quoted by Hammick and Mason (*loc. cit.*). All bond angles have been taken as tetrahedral, except in carbonium ions which have been taken as planar, and in quadrivalent atoms with two single bonds and one double bond which have also been taken as planar, with bonds at 120°. This is more in accordance with wave-mechanical results, and with the structures of benzene and ethylene (Coulson, *Quarterly Reviews*, 1947, **1**, 163).

in the formation of both semidines. But this is hard to reconcile with the fact that the *p*-semidine produced is derived, *e.g.*, in the case of *p*-ethoxyhydrazobenzene, by substitution of the phenetidine nitrogen into the aniline ring, whereas the *o*-semidine concurrently produced comes from the substitution of the aniline nitrogen into the phenetidine ring. This contrast is clear in Fig. 1, where R = OEt and R′ = H; the *o*-semidine union is *c*, whereas the *p*-semidine is *d*. It is to be noted that this distance in the activated state represented in Fig. 1 is 4·93 A., which is quite outside covalent- or ionic-bond length, and would imply ready fission.

A second important point in connection with the *p*-semidine transformation is that there is no recorded case of the change being brought about by the action of acid directly on a hydrazo-compound. In the 87 cases quoted by Jacobson (*loc. cit.*, pp. 90—99) all were carried out by the action of aqueous alcoholic stannous chloride and hydrochloric acid on azo-compounds. A single case (Barbier and Sisley, *Bull. Soc. chim.*, 1905, **33**, 1232) is recorded where zinc and sulphurous acid were substituted for stannous chloride. It thus becomes not only difficult to believe that the *p*-semidine transformation can be strictly analogous in mechanism to the other hydrazobenzene rearrangements, but it raises very definitely the question as to whether the presence of certain metallic ions is not crucial. We have attempted to effect a transformation by the action of hydrochloric acid on *p*-ethoxyhydrazobenzene, but the products were intractable. We have, however, found that when the reduction of appropriate azo-compounds is carried out in glacial acetic acid in the absence of metal ions, by the use of hydrogen and Raney nickel, no *p*-semidine is produced, but excellent yields of *o*-semidine are obtained. The case of 4-ethoxy-2′-methylazobenzene is particularly notable, because, when rearrangement is brought about by using stannous chloride in ethanol and hydrochloric acid, the main product is the *p*-semidine, and the separation of the small quantity of *o*-semidine is difficult (Jacobson, Franz, and Zaar, *Ber.*, 1903, **36**, 3860).

It is unprofitable to discuss mechanisms for the *p*-semidine transformation in terms of intermediate metallic complexes until more is known about its fundamental nature. There is as yet no direct evidence as to whether it is in fact intramolecular, or indeed whether it is a reaction of hydrazobenzenes at all. It appears to be certain that *p*-semidines cannot be produced by acids alone on hydrazobenzenes; moreover, under the conditions in which they are formed (reduction of azobenzenes in the presence of tin or zinc ions), considerable quantities of " fission bases " are also produced, and there is the possibility that *p*-semidines arise from catalysed interactions of Friedel–Crafts type.

EXPERIMENTAL.

The following 4-hydroxyazobenzene and corresponding compounds containing methyl groups were prepared by diazotisation and coupling by standard methods. The ethyl ethers were prepared by treatment of the hydroxy-compounds with sodium ethoxide and ethyl iodide, also by known methods: 4-hydroxyazobenzene, m. p. 152°, from ethanol; ethyl ether, m. p. 77°, from ethanol: 4-hydroxy-3-methylazobenzene, m. p. 128—129°, from ligroin; ethyl ether, m. p. 51°, from ethanol: 4-hydroxy-2′-methylazobenzene, m. p. 107°, from ethanol (Grandmougin and Freiman, *J. pr. Chem.*, 1908, **78**, 388, give m. p. 107—108°); m. p. 119°, from methanol or ligroin; ethyl ether, m. p. 51°, from ethanol; and 4-hydroxy-3 : 2′-dimethylazobenzene, m. p. 131°, from ethanol (Noelting and Werner, *Ber.*, 1890, **23**, 3259, give m. p. 132°), m. p. 148°, from methanol or ligroin; ethyl ether, m. p. 33°, from ligroin.

4-*Aminoazobenzene*. This was prepared by diazotisation of aniline and coupling of the product via diazoaminobenzene by standard methods; m. p. 122°, from ethanol.

Rearrangement experiments. Those by using stannous chloride were carried out more or less according to the methods described by Jacobson (*Annalen*, 1922, **428**, 85).

The ethoxy-azo-compound (1 g.) was dissolved in ethanol (20 c.c.) and a solution of stannous chloride (6 g.) in concentrated hydrochloric acid (20 c.c.) added. After ½ hour the mixture was made alkaline with 20% sodium hydroxide solution and filtered, and the residue dried and extracted with a mixture of toluene (1 part) and ligroin (3 parts). On cooling this solution, the *o*-semidine was usually obtained.

This method was used with some success on 4-ethoxyazobenzene and 4-ethoxy-3-methylazobenzene. The semidine from 4-ethoxy-3 : 2′-dimethylazobenzene was distilled at 2-mm. pressure in the absence of air.

The rearrangement of 4-ethoxy-2′-methylazobenzene was carried out as described by Jacobson, Franz, and Zaar (*loc. cit.*); it gave a yield of *o*-semidine corresponding to 3·5% of the original azo-compound.

Rearrangements by using the Raney nickel–acetic acid were carried out as follows. The azo-compound (2·0 g.) was dissolved in cold glacial acetic acid (30 c.c.) and Raney nickel (*ca.* 1 g.) added. Shaking the solution with hydrogen for five minutes ensured complete reduction, the actual decolorisation requiring only about two minutes. The catalyst was removed by filtration, water (100 c.c.) was added, and the bulk of the dilute acetic acid removed by distillation at 20-mm. pressure. The residue, after treatment with dilute sodium hydroxide solution, was extracted with ether, the extract dried (Na_2SO_4), and the ether removed. Two distillations under reduced pressure of the residue (without a leak which causes rapid oxidation) provided a separation from the lower-boiling fission bases (aniline, and *p*-phenetidine and homologues). The *o*-semidines distilled at 160—190°/0·05 mm; the colourless to pale yellow distillate solidified slowly on cooling, and was recrystallised from *cyclo*hexane. Yields were normally 30—35%, the remainder of the azo-compound being converted into fission bases.

The *o*-semidines are white solids, generally crystalline. Aerial oxidation of the solid is slow, but that of solutions is rapid. They were characterised by their benzil derivatives:

2-Amino-5-ethoxydiphenylamine, m. p. 94—95° (Jacobson and Fischer, *Ber.*, 1892, **25**, 995, give m. p. 95°); benzil derivative, m. p. 162° (Jacobson, *Ber.*, 1892, **25**, 1010, gives m. p. 161—162°): 2-amino-5-ethoxy-4-methyldiphenylamine, m. p. 94°; benzil derivative, m. p. 139° (Jacobson, *Annalen*, 1895, **287**, 135, 147, gives m. p. 94—95 for the amine and m. p. 136° for the benzil derivative); 2-amino-5-ethoxy-2′-methyldiphenylamine, m. p. 83°; benzil derivative, m. p. 170° (Jacobson, Franz, and Zaar, *loc. cit.*, give m. p. 82—83° for the amine and m. p. 172° for the benzil derivative); 2-amino-5-ethoxy-4 : 2′-dimethyldiphenylamine, m. p. 77°; benzil derivative, m. p. 150—153° (Jacobson, *Annalen*, 1895, **287**, 190, gives m. p. 78° for the amine and m. p. 153° for the benzil derivative).

DYSON PERRINS LABORATORY, OXFORD.

[*Received, March* 16*th*, 1950.]