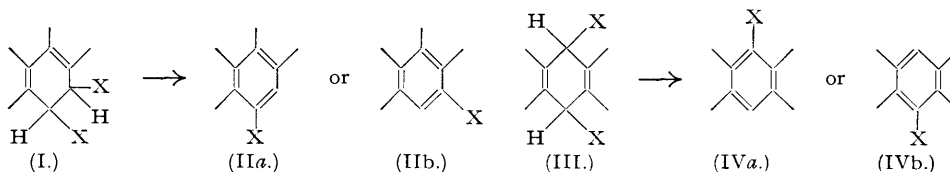


524. *An Interpretation of Some Elimination Reactions in Disubstituted Dihydro-derivatives of Aromatic Compounds.*

By G. M. BADGER.

The elimination of HX from disubstituted dihydro-derivatives of aromatic compounds (I and III) proceeds in such a direction that the remaining substituent is linked to the carbon atom which, in the parent compound, has the greater "electronic charge." In the aromatic compound obtained, the substituent is conjugated with the ring system to a greater extent than in the alternative structure. It is suggested that it is this greater degree of conjugation and consequent shortening and strengthening of the C-X bond which governs the direction of elimination.

ALTHOUGH aromatic compounds normally undergo *substitution* reactions, certain polycyclic aromatic compounds undergo *addition* reactions with very great facility, to give disubstituted dihydro-derivatives. These compounds are of two main types: first, that exemplified by the addition of halogens to phenanthrene and its derivatives (I), and secondly, that illustrated by similar additions to anthracene and its derivatives (III). The re-establishment of the aromatic structure, by elimination of either X₂, or of HX, often takes place spontaneously, but this is not invariably the case, some eliminations requiring the application of heat or the use of catalysts. The factors determining which of these reactions (elimination of X₂ or of HX) take place to the greater extent are not clearly understood (Bergmann and Weizmann, *J. Amer. Chem. Soc.*, 1938, 60, 1801). The present paper is concerned with the second reaction, and includes an interpretation of the *direction* of elimination of HX from unsymmetrical compounds of types (I) and (III). In such cases elimination can theoretically give rise to

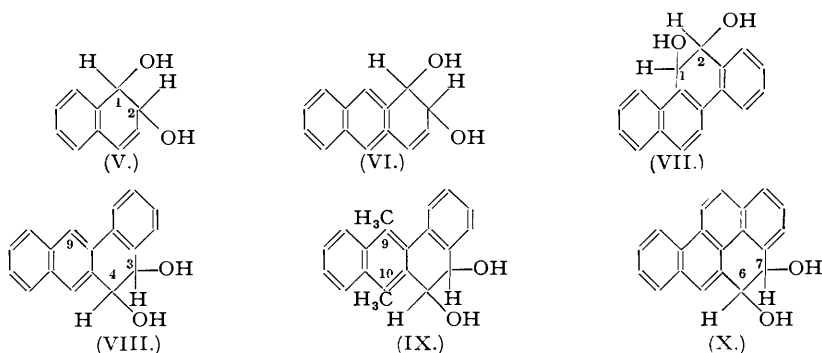


two alternative aromatic structures, namely (IIa or b) and (IVa or b). Examples of this type of elimination have been known for many years, especially in the phenanthrene and anthracene series, and attention has recently been directed to this problem by the work of Cook and Schoental (*J.*, 1948, 170) on the preparation and dehydration of some dihydro-diols of polycyclic compounds. In the great majority of cases, the elimination of HX has been shown to give only one of the theoretically possible aromatic structures. Evidence has now been accumulated that in all these examples the remaining substituent is linked to the carbon atom which, in the parent compound, has the greater "electronic charge." Expressed in quantum-mechanical terms, this is the carbon atom which has the greater index of free valence, and it is also the carbon atom normally attacked by electrophilic reagents.

Disubstituted dihydro-derivatives of aromatic compounds can exist in both *cis*- and *trans*-forms, but this circumstance appears to have no effect on the direction of elimination of HX and, indeed, appears to have no effect on whether (when this is possible) X₂ or HX is eliminated (Bergmann and Weizmann, *loc. cit.*). The dihydro-diols of aromatic compounds prepared by the action of osmium tetroxide followed by hydrolysis are almost certainly of *cis*-configuration (Criegee *et al.*, *Annalen*, 1936, **522**, 75; 1942, **550**, 99; Boeseken, *Rec. Trav. chim.*, 1922, **41**, 199), and a few dihydro-diols in which the configuration is almost certainly *trans*, have been isolated following metabolic oxidation of the parent hydrocarbons in rats and rabbits.

(±)-*trans*-1 : 2-Dihydroxy-1 : 2-dihydronaphthalene (V) has been obtained by metabolic oxidation of naphthalene in rabbits, and the (−)-form was obtained in similar experiments with rats. Both compounds are readily converted into 1-hydroxynaphthalene by elimination of H-OH under acidic conditions (Young, *Canad. Chem.*, 1946, **30**, 124; *Biochem. J.*, 1947, **41**, 417; Booth and Boyland, *Biochem. J.*, 1947, **41**, *Proc. xxix*). As is well known, the 1-position in naphthalene is more readily attacked by electrophilic reagents than is the 2-position. The indices of free valence for the two positions, calculated both by the valence-bond method (Daudel and Daudel, *J. Chem. Physics*, 1948, **16**, 639; Pullman, *Ann. Chim.*, 1947, **2**, 5), or by the molecular-orbital method (Coulson and Longuet-Higgins, *Rev. Sci.*, Paris, 1947, **85**, 929), show much greater values for the 1- than for the 2-position (see Table I), and the elimination of H-OH from (V) therefore takes place in such a direction that the phenolic hydroxyl group remains linked to the position with the greater index of free valence.

(±)-1 : 2-Dihydroxy-1 : 2-dihydroanthracene (VI) and the corresponding (−)-form have been obtained by metabolic oxidation of anthracene in rabbits and in rats, respectively. Both metabolites give rise to 1-hydroxyanthracene on dehydration (Boyland and Levi, *Biochem. J.*, 1935, **29**, 2679). The *meso*-(9 : 10)-positions are the most reactive centres in anthracene, but there is no doubt that, of the 1- and the 2-position, the former has the greater electronic charge. This is reflected in the indices of free valence (Table I).



1 : 2-Dihydroxy-1 : 2-dihydrochrysene (VII), prepared by the action of osmium tetroxide on the hydrocarbon and therefore almost certainly of *cis*-configuration, is known to give 2-hydroxychrysene on dehydration (Cook and Schoental, *loc. cit.*). Substitution of chrysene with electrophilic reagents also takes place at the 2-position (Newman and Cathcart, *J. Org. Chem.*, 1940, **5**, 618), and the 2-position has the greater index of free valence.

Elimination of H-OH from 3 : 4-dihydroxy-3 : 4-dihydro-1 : 2-benzanthracene (VIII), a dihydro-diol prepared from benzantracene with osmium tetroxide, gives 3-hydroxy-1 : 2-benzanthracene (Cook and Schoental, *loc. cit.*). No chemical evidence is available to indicate which of the two positions has the greater electronic charge. The fluorescence spectrum of 3-methyl-1 : 2-benzanthracene shows a much greater bathochromic shift than does that of its 4-methyl isomer (Schoental and Scott, *J.*, in the press), and, as is discussed below, this provides indirect evidence that the 3-position has a much greater electronic charge than the 4-position. Furthermore, the indices of free valence, by both methods of calculation, are slightly greater for the 3- than for the 4-position.

It was thought of interest to study the direction of elimination of H-OH from the dihydro-diols prepared from 9-methyl-1 : 2-benzanthracene and 9 : 10-dimethyl-1 : 2-benzanthracene by the action of osmium tetroxide. 3 : 4-Dihydroxy-9 : 10-dimethyl-3 : 4-dihydro-1 : 2-benzanthracene (IX) was prepared by the method of Cook and Schoental (*loc. cit.*), dehydrated by brief boiling with acetic acid containing a little hydrochloric acid, and the product methylated.

TABLE I.
Indices of free valence for polycyclic compound.

Compound.	Position.	Index of free valence.	
		V.-B. method.	M.-O. method.†
Naphthalene	1 *	0.122 <i>a</i>	0.40 <i>b</i>
	2	0.098	0.35
Anthracene	1 *	0.194 <i>a</i>	0.41 <i>b</i>
	2	0.161	0.36
Chrysene	1	0.190 <i>a</i>	0.388 <i>c</i>
	2 *	0.215	0.405
1 : 2-Benzanthracene	3 *	0.204 <i>a</i>	0.404 <i>c</i>
	4	0.200	0.403
9-Methyl-1 : 2-benzanthracene	3 *	0.187 <i>d</i>	—
	4	0.172	—
9 : 10-Dimethyl-1 : 2-benzanthracene	3 *	0.160 <i>d</i>	—
	4	0.139	—
3 : 4-Benzpyrene	6 *	—	0.40 <i>e</i>
	7 *	—	0.40

* Dehydration of the dihydro-diol proceeds in such a direction that the remaining phenolic hydroxyl group is linked to the position marked with an asterisk.

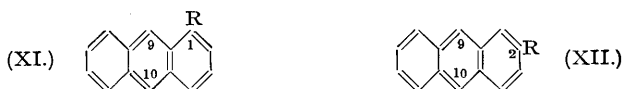
† The definitions used by the two methods are not identical.

a, Pullman, *Ann. Chim.*, 1947, **2**, 5. *b*, Coulson and Longuet-Higgins, *Rev. Sci. Paris*, 1947, **85**, 929. *c*, Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906. *d*, Dr. R. Daudel, private communication. *e*, Daudel, Daudel, and Vroelant, *Compt. rend.*, 1948, **227**, 1033.

This product was shown to be 3-methoxy-9 : 10-dimethyl-1 : 2-benzanthracene as, on oxidation with sodium dichromate, it gave 3-methoxy-1 : 2-benzanthraquinone, identified by comparison with an authentic specimen. Similarly, 9-methyl-1 : 2-benzanthracene gave, with osmium tetroxide, 3 : 4-dihydroxy-9-methyl-3 : 4-dihydro-1 : 2-benzanthracene, converted by dehydration and methylation into 3-methoxy-9-methyl-1 : 2-benzanthracene, the orientation of which was confirmed by oxidation to 3-methoxy-1 : 2-benzanthraquinone. With both of these compounds the 3- has a greater index of free valence than the 4-position (Table I). It must be admitted, however, that on general grounds one would expect the 9-methyl group of 9-methyl-1 : 2-benzanthracene to activate the 4-position. Evidently the 3-position of 1 : 2-benzanthracene has a very much greater negative character than the 4-position.

Several other dihydro-diols have been prepared and dehydrated to phenols, but in these cases the evidence at present available does not indicate which of the two positions has the greater charge. Cook and Schoental (*loc. cit.*) found that with the 6 : 7-dihydro-diol of 3 : 4-benzpyrene (X), dehydration gave a mixture of phenols, apparently 6- and 7-hydroxy-3 : 4-benzpyrene. The 6- and the 7-position of 3 : 4-benzpyrene are therefore approximately equivalent, in spite of the fact that this hydrocarbon is not symmetrical. The indices of free valence, determined by an approximate molecular-orbital method, are indeed of the same magnitude (Daudel, Daudel, and Vroelant, *Compt. rend.*, 1948, **227**, 1033), but this is probably a fortuitous circumstance. The 3- and the 4-position of 1 : 2 : 5 : 6-dibenzanthracene are likewise found to have the same index of free valence, but dehydration of the 3 : 4-dihydro-diol of this compound (Cook and Schoental, *loc. cit.*) leads to only one phenol, the orientation of which has not been determined.

The direction of elimination in 9 : 10-addition compounds of 1- or 2-substituted anthracenes might be expected to be governed by the electronic character of the substituent. The *meso*-positions of anthracene are so much more reactive than the positions in the benz rings that only the most powerful orientating groups (OH, NH₂, etc.) can direct substituents into these rings rather than into the *meso*-positions. In the great majority of cases, addition to the *meso*-positions takes place to give a 9 : 10-dihydro-derivative which then undergoes (either spontaneously or by suitable treatment) elimination of X₂ or of HX to give the aromatic structure.



With 1-substituted anthracenes (XI), the 9-position (which is separated from R by three carbon atoms) resembles a *meta*-position in a benzene derivative, whilst the 10-position (which is separated from R by either four or six carbon atoms depending on the route) resembles a *para*-position. If R is deactivating or *meta*-directing, substitution must give the 9-substituted

derivative, and a 9:10-addition compound will be expected to decompose by elimination of HX to give the 9-substituted derivative. On the other hand, if R is an activating, or *ortho-para*-directing group, substitution, or addition followed by elimination, must give the 10-substituted derivative. Similarly, with the 2-substituted anthracenes (XII), the 9-position (distant by four carbon atoms from R) takes on the character of a *para*-position, and the 10-position resembles a *meta*-position (distant by five carbon atoms from the substituent) (cf. Pullman, *Bull. Soc. chim.*, 1948, **15**, 533). When R is *ortho-para*-directing, elimination of HX will be expected to give 9-substituted derivatives, and when R is *meta*-directing the weak orientating influence will tend to give 10-substituted derivatives.

In many cases, the orientation of the derivatives obtained as above has not been rigidly established. When this has been done, however, the results are in agreement with the above generalisations. 1-Chloroanthracene and bromine give an addition compound, which is converted in boiling xylene into 1-chloro-10-bromoanthracene by elimination of hydrogen bromide (Cook, *J.*, 1928, 2798). The +*T* effect of the 1-chloro-substituent is clearly the controlling factor. Similarly, in the Friedel-Crafts reaction it is known that 1-chloroanthracene reacts in the 10-position (Liebermann, *Ber.*, 1912, **45**, 1186; Cahn, Jones, and Simonsen, *J.*, 1933, 444). Further, it is known that in the Friedel-Crafts reaction both 2-methyl- and 2-chloro-anthracene react in the 9-position as expected (Butescu, *Ber.*, 1913, **46**, 212; Mayer, Fleckenstein, and Gunther, *Ber.*, 1930, **63**, 1464; Dansi and Sempronj, *Gazzetta*, 1936, **66**, 182). Where the orientation has not been established, it is possible to decide which of the alternative structures is the more probable. For example, the product obtained by elimination of hydrogen bromide from the 9:10-dibromide of methylanthracene-1-carboxylate is almost certainly the 9- and not the 10-bromo-compound as was assumed by Coulson (*J.*, 1930, 1931) after consideration of the theory advanced by Barnett and Wiltshire (*Ber.*, 1929, **62**, 3063) but later admitted by Barnett and Low (*Ber.*, 1931, **64**, 49) to be erroneous.

Discussion.—It is well known that C-Cl, C-OH, C-CH₃, and other linkages in aromatic compounds are significantly shorter than corresponding linkages in aliphatic compounds (Brockway and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2181; Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, **167**, 122), and this shortening of the bond may be taken as a measure of the extent of conjugation of the substituent with the ring. By the valence-bond method this is usually interpreted in terms of resonance between the various possible ionic structures in which the substituent is linked to the ring with a double bond. Isomeric derivatives of di- and polycyclic systems do not always have the same number of structures showing such conjugation: with 1-substituted naphthalenes, for example, there are seven such structures to be taken into consideration, and only six structures for 2-substituted derivatives. It is therefore to be expected that a substituent in the 1-position of naphthalene will be conjugated with the ring to a greater extent than the same substituent in the 2-position, and the experimental evidence supports this conclusion. Examination of the dipole moments of the halogenated naphthalenes has shown that the C-Cl bond in 1-chloronaphthalene has about 14.2% double-bond character, as against 13.0% for the isomeric 2-chloronaphthalene (Ketelaar and Oosterhout, *Rec. Trav. chim.*, 1946, **65**, 448).

It has also been claimed that the magnitude of the shift in wave-length of the absorption bands (and fluorescence bands), which results by the introduction of a substituent at various positions in the molecule (bathochromic shift), is associated with the extent of conjugation of the substituent with the ring. The shift in wave-length of the absorption bands for 1-substituted naphthalenes is always greater than that for isomeric 2-substituted derivatives; and in the anthracene series a substituent in a *meso*-position produces a greater shift than the same substituent in position 1, and this in turn is greater than the bathochromic shift produced by the same substituent in the 2-position. These observations are particular examples of the generalisation derived by Pullman (*Compt. rend.*, 1946, **222**, 1396), that in any given molecule the extent of conjugation of a substituent with the ring is always greatest when this substituent is linked to the carbon atom having the greatest index of free valence. In the methylbenzanthracenes, it has been shown that there is a good correlation between the magnitude of the bathochromic shift, the extent of conjugation, and the index of free valence at the carbon atom to which the substituent is linked (Pullman, *Compt. rend.*, 1947, **224**, 1354; see also Pullman, *Bull. Soc. chim.*, 1948, **15**, 533; Daudel and Martin, *ibid.*, p. 559). Moreover, Kiss, Molnar, and Sandorfy (*Compt. rend.*, 1948, **227**, 724) have pointed out that the magnitude of the shift in the absorption bands produced by hydroxyl, methoxyl, and methyl groups may be correlated with the degree of conjugation of these groups determined by other methods. It is also of interest that the shift in the absorption bands of chlorobenzene as compared with that

of benzene, as Price and Walsh (*Proc. Roy. Soc.*, 1947, A, **191**, 22) have pointed out, provides evidence that the conjugation of ring π electrons with the chlorine occurs even without the approach of another molecule.

There seems to be no doubt, therefore, that disubstituted dihydro-derivatives of aromatic compounds decompose by elimination of HX in such a direction that the substituent remains linked to the carbon atom having the greater index of free valence, and that a substituent at this position is conjugated with the ring to a greater extent than at the alternative position of lower index of free valence. In the aromatic structure formed by the elimination the C-X bond is therefore shorter and stronger than in the other theoretically possible structure, and it is these factors which appear to govern the direction of elimination.

EXPERIMENTAL.

3 : 4-Dihydroxy-9-methyl-3 : 4-dihydro-1 : 2-benzanthracene.—9-Methyl-1 : 2-benzanthracene was prepared by the method of Cook, Robinson, and Goulden (*J.*, 1937, 393). The hydrocarbon (1 g.) was added to a solution of osmium tetroxide (1 g.) in benzene (25 c.c.) and pyridine (1 c.c.) at room temperature. After 3 days, the complex was precipitated by addition of light petroleum. The solid was collected, washed with light petroleum, dried in air, and then hydrolysed by shaking it (3 hours) with 1% aqueous potassium hydroxide containing 10% of mannitol, in the presence of methylene chloride (cf. Cook and Schoental, *loc. cit.*). The organic layer was separated, washed, dried, and evaporated. **3 : 4-Dihydroxy-9-methyl-3 : 4-dihydro-1 : 2-benzanthracene**, obtained in almost theoretical yield, crystallised from benzene in small colourless needles which melted with decomposition at 130° (rapid heating) (Found: C, 82.7; H, 5.9. $C_{19}H_{16}O_2$ requires C, 82.6; H, 5.8%).

3-Methoxy-9-methyl-1 : 2-benzanthracene.—A solution of the diol (0.1 g.) in acetic acid (3 c.c.) and 2 drops of concentrated hydrochloric acid was boiled for 2 minutes, cooled, and diluted with water. The crude phenol was immediately methylated with methyl sulphate and sodium hydroxide at 100°. The product was collected, dissolved in light petroleum (b. p. 60–80°), and separated from some resinous material by passage through a column of alumina. The resinous material was strongly adsorbed, and the elution of the desired product (with light petroleum) was followed by irradiation with ultra-violet light. **3-Methoxy-9-methyl-1 : 2-benzanthracene** formed colourless clusters of plates, m. p. 124–125° from light petroleum (Found: C, 88.6; H, 5.7. $C_{20}H_{16}O$ requires C, 88.2; H, 5.9%). The above compound (0.1 g.) was oxidised by boiling with sodium dichromate (0.5 g.) in glacial acetic acid (5 c.c.) for $\frac{1}{2}$ hour. After addition of water the 3-methoxy-1 : 2-benzanthraquinone was collected and recrystallised from alcohol. It had m. p. 188–189°, not depressed by an authentic specimen of the same m. p., prepared by the method of Fieser and Dietz (*J. Amer. Chem. Soc.*, 1929, **51**, 3141).

3-Methoxy-9 : 10-dimethyl-1 : 2-benzanthracene.—The dihydro-diol obtained by the action of osmium tetroxide on 9 : 10-dimethyl-1 : 2-benzanthracene was dehydrated, and the product methylated by the method of Cook and Schoental (*loc. cit.*). The orientation of this methoxydimethylbenzanthracene (0.1 g.) was proved by its oxidation with sodium dichromate (0.5 g.) in boiling acetic acid. After purification by chromatography and recrystallisation from alcohol, the 3-methoxy-1 : 2-benzanthraquinone was identified by m. p. and mixed m. p. 188–189°.

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