138. *A Theoretical Treatment of the Diels–Alder Reaction. Part I. Polycyclic Aromatic Hydrocarbons.*

By R. D. Brown.

A new theoretical treatment of the diene synthesis is described. A quantity termed the para-localisation energy is defined, and the results of calculations of this quantity for various pairs of positions in some polycyclic aromatic hydrocarbons are reported. It is shown that these values can be used to predict correctly in every case whether a molecule is reactive, and the observed position of addition. The need for some experimental rate measurements is briefly indicated and the factors neglected and approximations involved in the proposed theory are enumerated.

The mechanism of the Diels–Alder reaction has been the subject of a number of investigations. In particular it has been shown by stereochemical and kinetic evidence (Bergmann and Eschinazi, *J. Amer. Chem. Soc.*, 1943, **65**, 1405; Wassermann, *J.*, 1942, 612) that the activated complex has a configuration similar to that of the final addition product, *i.e.*, that the two new C–C bonds are formed simultaneously. Theoretical interpretations include Clar's (*Ber.*, 1931, **64**, 2194; 1932, **65**, 1521) involving biradical intermediates; an alternative explanation applicable vinyl derivatives of aromatic hydrocarbons has been proposed more recently (Daudel and Pullman, *J. Physique*, 1946, **7**, 105; *Compt. rend.*, 1945, **221**, 201; Daudel *et al.*, *Bull. Soc. chim.*, 1948, **15**, 1202), the dienic properties being associated with certain features of the molecular diagrams obtained by the method of mesomerism. However it is hard to see how either of these ideas could be applied semiquantitatively to determine relative reactivities of various molecules.

Evans and Warhurst (*Trans. Faraday Soc.*, 1938, **34**, 614) have given a detailed treatment of the kinetics of the dimerisation of butadiene, based on the theory of absolute reaction rates, and assuming the configuration of the activated complex mentioned above. Unfortunately more complex systems are not so susceptible to such a treatment.

The proposed theory combines the advantages of a semiquantitative treatment with applicability to a wider range of molecules. In many ways it is analogous to Wheland's treatment of aromatic substitution (*J. Amer. Chem. Soc.*, 1942, **64**, 900; Dewar, *J.*, 1949, 463). For the present we shall consider the addition of one particular dienophil (maleic anhydride) to various conjugated hydrocarbons; it is hoped later to extend the theory to cover the reactions of various dienophils with a particular hydrocarbon.

Assumptions of the Theory.—The formation of an adduct involves the localisation of two of the π-electrons of the conjugated hydrocarbons to form the two new σ C–C bonds. The fundamental assumption of the theory is that the ease of formation of an adduct at a pair of atoms, *m* and *n*, of the hydrocarbon depends only on the energy required to localise two of the π-electrons upon atoms *m* and *n*, *provided that* m *and* n *are orientated favourably*. This latter provision will be taken to be that *m* and *n* must lie para to one another in the case of a polycyclic hydrocarbon. It is proposed to term this energy quantity the *para-localisation energy* * of the pair of atoms *m* and *n*.

The above assumption is equivalent to assuming that the entropy of activation is constant for a given dienophil, and that the important variable part of the potential energy of activation is the para-localisation energy. If such assumptions are valid then it is also likely that the para-localisation energy is the important variable portion of the free energy of reaction; in other words it is likely that the products most rapidly formed will be the most stable. This " consequence " is important because in many cases it is not clear whether the experimentally isolated products are those most rapidly formed or those which are the most stable (from the equilibrium point of view); for the present theory we are justified in interpreting qualitative results in either of these two ways.

Computation of Para-localisation Energies.—The para-localisation energies may be computed by any of the standard approximate quantum-mechanical methods, but the molecular-orbital method, which has several advantages over other methods, particularly when large unsymmetrical molecules are concerned, has been used exclusively in the present work. Clearly from the definition of the para-localisation energy, *P*, we have :

$$P = E_r - E + 2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the π-electron energy of the original conjugated system, 2α the energy of two isolated π-electrons, and E_r is the total π-electron energy of the one or more separate conjugated systems left when the two π-electrons are localised upon atoms *m* and *n*. In keeping with previous terminology (Brown, *Aust. J. Sci. Res.*, *A*, 1949, **2**, 566) these conjugated systems will be termed collectively the residual molecule.

The energies E, E_r may be computed by assuming orthogonal atomic orbitals, or by including the overlap integral, whose value is generally assumed to be 0·25. The latter procedure is generally accepted as being more accurate, and it has been proposed (Brown, *Trans. Faraday Soc.*, in the press) to denote energy quantities computed by assuming an overlap integral of 0·25 by primed symbols, quantities computed by assuming orthogonal orbitals being represented by the corresponding unprimed symbols. In addition the former quantities are expressed in terms of the exchange integral, γ, the latter in terms of the exchange integral, β. Thus P', defined by

$$P' = E_r' - E' + 2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will be expressed in terms of γ, P, defined by equation (1), in terms of β. In general both P and P' will be listed for each pair of positions, but only P' will be converted into kcal. mol.$^{-1}$, the

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* I am indebted to Professor C. A. Coulson for suggesting this name and the symbol *P*.

conversion factor, $\gamma = -34$ kcals., recommended by Dewar (*Trans. Faraday Soc.*, 1946, **42**, 767) being used for this purpose.

P and P' may alternatively be expressed in terms of resonance energies :

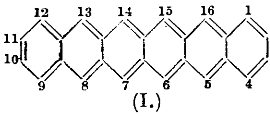
$$P = R - R_r - 2\beta \tag{3}$$

$$P' = R' - R_r' - 1{\cdot}6\gamma \tag{4}$$

Before proceeding to the discussion of results obtained for various molecules we may notice a general principle which is apparent from inspection of equations (3) and (4), namely that for any given molecule the most reactive pair of positions will be those giving rise to the most stable residual molecule.

Results.—The results of calculations of P and P' are listed in Tables I—IV. Except where otherwise indicated in the Tables, the resonance energies involved have been calculated by direct solution of the relevant secular determinants. Differences in P' from the value $-2{\cdot}07\gamma$ for the 9 : 10 positions of anthracene have in many cases been converted into " theoretical " ratios of rate constants upon the assumption that $\boldsymbol{R}T = 0{\cdot}6$ kcal. N represents the number of separate conjugated systems comprising the residual molecule. This will be referred to again later.

The para-localisation energies of the linear polyacenes (I) are shown in Table I. Two things are apparent. First the para-localisation energy of the most reactive pair of positions for a given molecule decreases with increasing size of the molecule, pointing to an increase in reactivity with increasing molecular weight. Secondly in any particular molecule the reactivity of successive pairs of " meso "-positions (pairs such as 1 : 4, 5 : 16, 6 : 15 in hexacene being classed as " meso " for convenience in discussion) increases as we move towards the centre of the molecule. From the results for an infinite strip it is clear that a limiting value of the reactivity is rapidly approached in both of these sequences.



(I.)

Many other possible pairs of positions have been excluded from consideration in the Tables by means of the principle that only pairs giving rise to sufficiently stable residual molecules will be reactive, and, on this qualitative principle, the positions listed are the most reactive of all possible pairs in each molecule.

TABLE I.

The Polyacenes.[a]

			P',		Relative
Molecule.	Positions.	$P(-\beta)$.	$(-\gamma)$.	kcals.	rate.
Benzene	1 : 4	4·00	2·67	91	*ca.* 10^{-15}
Naphthalene	1 : 4	3·68	2·40	82	*ca.* 10^{-8}
Anthracene	1 : 4	3·63	2·34	80	*ca.* 10^{-7}
	9 : 10	3·31	2·07	70	1
Naphthacene	1 : 4	3·62	2·33	79	—
	5 : 12	3·25	2·01	68	30
Pentacene	1 : 4	3·61	2·33	79	—
	5 : 14	3·23	1·99	68	90
	6 : 13	3·18	1·94	66	1,600
Hexacene (I)	1 : 4	3·61	2·33	79	—
	5 : 16	3·23	1·99	68	90
	6 : 15	3·16	1·92	65	5,000
Infinite strip [b]	*a*	3·611	2·325	79	—
	b	3·223	1·984	67	—
	c	3·151	1·913	65	—
	d	3·132	1·893	64	—
	e	3·126	1·887	64	—
	f	3·124	1·885	64	—
	g	3·124	1·884	64	48,000

[a] N is 2 for all pairs of positions considered here. [b] Values for the limit of the polyacene series were computed by using asymptotic values for the resonance energies, R, R' (results in course of publication). The pairs of positions referred to by *a*, *b*, *c*, . . . are the successive " meso "-positions starting at one end of the strip; for example, on this system the pairs of positions in hexacene numbered 1 : 4, 5 : 16, 6 : 15 would be referred to as *a*, *b*, *c*, respectively.

The results given in Table I explain the experimental findings for the polyacenes. As benzene and naphthalene do not add maleic anhydride (Mameli, Pancotto, and Crestani, *Gazzetta*, 1937, **67**, 669; Alder, " Newer Methods of Preparative Organic Chemistry," 1948, p. 485; Clar, " Aromatische Kohlenwasserstoffe," 1941, p. 12) and anthracene on the other hand undergoes addition at the 9 : 10-positions (Clar, *Ber.*, 1931, **64**, 1682; *op. cit.*, p. 126; Diels and

Alder, *Annalen*, 1931, **486**, 191) it appears that appreciable addition can be detected only when P is less than $-3{\cdot}6\beta$ or P' is less than $-2{\cdot}3\gamma$ (78 kcals./mole). In agreement with prediction naphthacene, pentacene, and hexacene add maleic anhydride at the central " meso "-positions with rapidly increasing ease (Clar, *Ber.*, 1932, **65**, 503; 1931, **64**, 2194; 1939, **72**, 1817).

The critical values of P and P' just mentioned will be seen to predict correctly the course of the Diels–Alder reaction for all polynuclear hydrocarbons for which the experimental facts are known. Strictly, a given critical value of P' should apply only for a given experimental temperature (and possibly solvent) and for a given value of N. However, in the present paper almost all reactive positions correspond to $N = 2$. Also it might be necessary to specify different critical values for different dienophils. The experimental data are not sufficiently numerous to select any particular temperature as standard.

TABLE II.

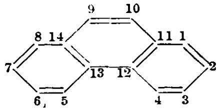
Molecule.	Positions.	N.	$P(-\beta)$.	P', $(-\gamma)$.	P', kcals.
Phenanthrene (II)	1 : 4	2	3·77	2·47	84
	9 : 12	2	4·46	2·88	98
	2 : 12	2	4·51	2·91	99
	4 : 5	1	4·37 [a]	—	—
Chrysene (III)	3 : 6	2	3·74	2·45	83
	8 : 16	2	4·33 [b]	—	—
	7 : 13	2	4·52	2·94	100
	6 : 7	1	4·57 [c]	—	—
3 : 4-Benzphenanthrene (IV)	1′ : 4′	2	3·74	2·45	83
	2 : 12	2	4·25	2·70	92
	1 : 4	2	4·52	2·93	100
	4′ : 13	1	5 [c]	—	—
Picene (V)	1 : 4	2	3·75	2·46	84
	6 : 16	2	4·51	2·92	99
	6 : 7	1	*ca.* 3·80 [c]	—	—
	1 : 14	1	*ca.* 3·97 [c]	—	—

[a] The resonance energy of the residual molecule, R_r, was obtained from Syrkin and Diatkina's data (*Acta Physicochim.*, 1946, **21**, 641). [b] R_r was obtained from Berthier and Pullman's data (*Bull. Soc. chim.*, 1948, **15**, 554). [c] R_r was calculated from the redox potential of the corresponding quinone by an empirical method (in course of publication).

The para-localisation energies of some angular hydrocarbons are listed in Table II. All values listed are greater than those for 1 : 4-addition to naphthalene; this is in agreement with experimental observations (Jones, Gogek, and Sharpe, *Can. J. Research*, *B*, 1948, **26**, 719; Alder, *op. cit.*, p. 485; Clar, *Ber.*, 1932, **65**, 853; Clar and Lombardi, *ibid.*, p. 1413) that phenanthrene and chrysene will not react with maleic anhydride. The possibility of reaction of 3 : 4-benzphenanthrene or picene with maleic anhydride does not seem to have been investigated. The present results indicate that no addition will take place with these hydrocarbons; a result to be expected from the principle that " only molecules containing the anthracene skeleton will react." It will also be noticed that the reactivity, as indicated by the smallest value of the para-localisation energy for each molecule, remains almost constant.

Values of P and P' for some molecules related to anthracene are presented in Table III (it will be noticed that N is 2 for all pairs of positions considered). These indicate that addition will occur in each case, the " meso "-positions of the anthracene portions being attacked preferentially, and the ease of addition decreasing in the sequence : 1 : 2-benznaphthacene, anthracene, 4 : 5-benzchrysene, 1 : 2-benzanthracene, pentaphene, 1 : 2-3 : 4-dibenzanthracene, 1 : 2-7 : 8-dibenzanthracene, 1 : 2-5 : 6-dibenzanthracene, the last two being of almost identical reactivity (calculations to a greater number of significant figures for P' predict relative reaction rates of 1 : 1·07 for these two compounds) so that the actual relative reactivities will probably be more dependent upon factors which are ignored in the present treatment for simplicity (*e.g.*, entropy of activation). This sequence agrees with all available experimental facts. 1 : 2-Benzanthracene is more difficultly reactive than anthracene (Clar, *Ber.*, 1932, **65**, 519; "Aromatische Kohlenwasserstoffe," p. 133), in sharp contrast to its isomer, naphthacene (see above). This is

(II.)



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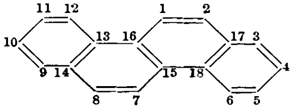


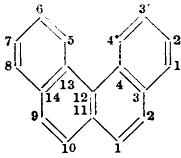
TABLE III.

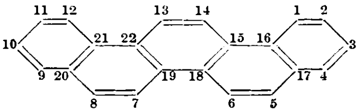
Molecule.	Positions.	$P(-\beta)$.	P',		Relative rate.
			$(-\gamma)$.	kcals.	
Anthracene	1 : 4	3·63	2·34	79	—
	9 : 10	3·31	2·07	70	1
1 : 2-Benzanthracene [a]	1′ : 4′	3·78	2·49	85	—
	5 : 10	3·41	2·17	74	0·003
	6 : 9	3·64	2·36	80	—
1 : 2-3 : 4-Dibenzanthracene	1′ : 4′	3·83	2·55	87	—
	5 : 10	3·49	2·24	76	0·00006
	6 : 9	3·70	—	—	—
1 : 2-5 : 6-Dibenzanthracene	1′ : 4′	3·79	2·49	85	—
	5 : 10	3·51	2·26	77	0·00002
1 : 2-7 : 8-Dibenzanthracene	1′ : 4′	3·79	2·49	85	—
	5 : 10	3·51	2·26	77	0·00002
Pentaphene (2 : 3-6 : 7-dibenzphenanthrene)	1 : 4	3·67	2·38	81	—
	5 : 14	3·45	2·20	75	0·0006
1 : 2-Benznaphthacene [a]	1′ : 4′	3·80	2·49	85	—
	5 : 12	3·36	2·11	72	0·1
	6 : 11	3·28	2·03	69	10
	7 : 10	3·64	2·34	79	—
4 : 5-Benzchrysene [a]	9 : 12	3·74	2·45	83	—
	3 : 6	3·38	2·14	73	0·02
	1′ : 4′	3·64	2·36	80	—

[a] The resonance energies of these compounds were computed by using an empirical method based upon the concept of " annelation energy " (in course of publication).

an excellent example of the different effects of linear and angular annelation upon the resonance energy of a polycyclic hydrocarbon (the residual molecule is the same for " meso "-addition to these two hydrocarbons), and can be shown to be related to the difference in mobile order of the 1 : 2- and the 2 : 3-bond in anthracene (results in course of publication). 1 : 2-5 : 6-Dibenzanthracene reacts considerably less readily than anthracene with maleic anhydride (Cook, *J.*, 1931, 3273), and pentaphene adds two molecules of maleic anhydride at a much slower rate than anthracene, at the positions predicted in Table 3 (Clar, *Ber.*, 1931, **64**, 2195). It will be observed that addition of one molecule of maleic anhydride to the 5 : 14-positions of pentaphene results in a molecule of adduct which in the present treatment must be regarded as anthracene; thus the second addition occurs at the " meso "-positions in the anthracene system, which corresponds to the 8 : 13-positions in the pentaphene system, and so must be expected to take place more rapidly than the addition of the first molecule of dienophil. The experimental data for 1 : 2-benznaphthacene, 4 : 5-benzchrysene, and 1 : 2-3 : 4-dibenzanthracene are also in excellent accord with the theory. Clar and Lombardi (*ibid.*, 1932, **65**, 1419) noted qualitatively that the order of reactivity is that predicted by the present theory. The relative rates deduced from differences in P' will be noticed to be 1,000,000 : 2,000 : 1 but these are expected to be too great because complete localisation is assumed in the activated complex. This makes the calculated values

(IV.)





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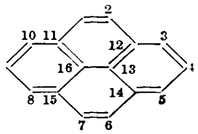

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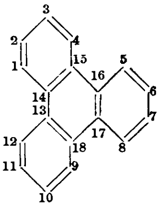

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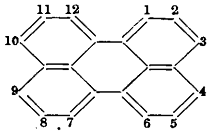

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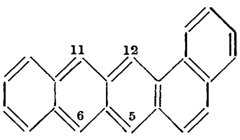

(IX.)

of P' too great and the effect is not wholly cancelled when differences in P' are considered. Hence when these are converted into kcals. with the conversion factor which is known (Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767) to give excellent values for resonance energies, the resultant differences in activation energy will necessarily be too great. The predicted relative rates are of course exponential functions of the activation-energy differences and so are very sensitive to the absolute magnitudes of the latter. This could be overcome by choosing a value for γ which gives satisfactory relative rates, but in view of the approximations inherent in the present treatment it is unlikely that anything more reliable than the order of magnitude of relative rates could be estimated by this method. In this connection comparative measurements of the rates of addition for some of the hydrocarbons listed in Table III would be valuable, and the case of 1 : 2-7 : 8- and 1 : 2-5 : 6-dibenzanthracene is particularly interesting in view of the very slight difference (0·0012γ) in P' for these two compounds (see above).

The theoretical results for 1 : 2-benznaphthacene, in addition to predicting the correct reactivity relative to the other related molecules, also lead to the correct conclusion about the position of addition. Thus of the two possible pairs of positions, shown in (IX), which are expected to be reactive on empirical grounds, it is 6 : 11 which undergoes addition, as the present theory predicts. This could not have been predicted by the existing empirical principles.

TABLE IV.

Molecule.	Position.	N.	$P(-\beta)$.	P', $(-\gamma)$.	P', kcals.
Diphenyl	1 : 4	3	4·38	2·78	95
	2 : 5	2	3·96	2·64	90
	2 : 2′	1	4·33	3·01	102
p-Terphenyl [a]	1 : 4	3	4·39	2·79	95
	2 : 5	2	3·96	2·64 [b]	90
	2′ : 5′	2	3·92	2·62	89
p-Quaterphenyl [a]	1 : 4	3	4·39	2·79	95
	2 : 5	2	3·96 [c]	2·64 [c]	90
	2′ : 5′	2	3·92	2·61	89
Pyrene (VI)	3 : 14	2	4·38 [d]	2·79 [d]	95
	6 : 16	1	4·50 [d]	2·93 [d]	100
	11 : 12	2	5·43 [e]	—	—
Triphenylene [e] (VII)	1 : 4	2	3·79	—	—
	2 : 15	2	4·42	—	—
	13 : 16	2	5·19	—	—
	1 : 12	1	4	—	—
Perylene (VIII)	1 : 12	1	3·92 [d]	2·60 [d]	88

[a] The resonance energies of these molecules were computed from the empirical equations for the conjugation energies (Brown, *Aust. J. Sci. Res.*, *A*, 1949, **2**, 566; other results in course of publication). [b] R' for the residual molecule was calculated from the empirical equation for the conjugation energy, C'. [c] The conjugation energies, C and C', were estimated for calculation of R and R'. [d] The resonance energies of the residual molecules, R_r, R_r', were calculated from C and C'. [e] The value used for the resonance energy of this molecule was that given by Syrkin and Diatkina (*loc. cit.*).

The para-localisation energy of some miscellaneous hydrocarbons are presented in Table IV. From the critical values for P and P' suggested above it would be expected that none of the molecules listed would add maleic anhydride. The experimental observations agree with this prediction in the case of diphenyl and pyrene (Arbuzov, Salmina, and Sharpshinskaya, *Trans. Butlerov Inst. Chem. Tech. Kazan*, 1934, No. 2, 9; Clar, *Ber.*, 1936, **69**, 1683) but at first sight the reaction reported for perylene (Clar, *ibid.*, 1932, **65**, 846) appears to form an exception to the present theory. However it is significant that the product isolated is not the adduct but the corresponding dehydrogenated compound. It seems likely that the factor which produces this product is an irreversible disturbance of the equilibrium between the adduct and its components (and very much in favour of the components as judged by the value of P') by oxidation by the solvent, nitrobenzene. Further weight is lent to this interpretation by Clar's observation that no detectable reaction occurs in boiling xylene, and also that prolonged heating at the relatively high temperature of boiling nitrobenzene was required to obtain a satisfactory reaction.

It may be remarked in passing that the lack of reactivity noted for some of the other molecules considered above may be due to the setting up of an unfavourable equilibrium just as much as due to a very small rate constant because if the value of P or P' is a satisfactory criterion these two phenomena will run parallel (see above).

The above study of some 24 hydrocarbons shows that the proposed theory of the Diels–Alder reaction is completely satisfactory to the present extent of experimental knowledge. The empirical fact that molecules containing the anthracene skeleton are in general reactive and the more angular molecules unreactive is convincingly explained by the fact that the former can give rise to relatively stable residual molecules whereas the latter cannot. In addition the relative reactivities of reactive hydrocarbons can readily be interpreted; indeed it is possible to interpret these relative reactivities in a general qualitative way, as will be described in a later paper of this series.

Approximations and Neglected Factors.—As mentioned above, variations in the entropy of activation are neglected in the present theory, variations in reaction rate being assumed to be due only to variations in the potential energy of activation. Formation of the activated complex will presumably involve partial localisation of two of the π-electrons of the hydrocarbon, together with two of its carbon atoms, m and n, which are now linked to the dienophilic portion by incipient σ-bonds. The energy of activation will include the energy of formation of the latter bonds together with energy changes accompanying any change in the spatial configuration of the hydrocarbon portion. The assumption has been made that any such contributions are approximately constant from molecule to molecule, and attention has then been focussed upon variation in the π-electron energy changes.

As the atoms m and n are not completely localised in the transition state the residual molecule will be more stable than has been assumed above by an amount equal to the conjugation energy of the various separate conjugated systems through atoms m and n. Qualitatively we might expect this conjugation energy to increase with increase in N, the number of separate systems comprising the residual molecule. Consequently if two pairs of positions have the same para-localisation energy we should expect the one with the greater N to be the more reactive.

Another approximation involved in the present theory is the calculation of the para-localisation energy by an approximate method. However the systems involved are always neutral molecules and Dewar (*Trans. Faraday Soc.*, 1946, **42**, 767) has shown that the molecular-orbital method gives very satisfactory resonance energies in such cases. It will be observed that the proposed theory applies equally well to the " ionic " mechanism favoured by Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 3058) for the diene synthesis. In the latter case we have merely to replace the assumption that a system of two isolated carbon atoms, each carrying one π-electron, has an energy approximately constant from molecule to molecule, by the analogous assumption that a system of two isolated carbon atoms, one carrying two π-electrons, the other none, has the same property. For convenience the energy of either system may be assumed to be 2α to simplify the values of P and P'.

The para-localisation-energy concept has been applied to some other polycyclic hydrocarbons for which the experimental investigation has not been made. These results and others for vinyl and phenyl derivatives of aromatic hydrocarbons will be presented in Part II.

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