## **360.** *The Mechanism of Additions to Double Bonds. Part II. The Steric Course of Two Diene Syntheses.*

By Albert Wassermann.

The addition products of benzoquinone or maleic anhydride with *cyclo*pentadiene can exist in geometrically isomeric forms, the rates of formation of which are different. The purpose of this paper is to explain this difference.

*The Addition of Benzoquinone to* cyclo*Pentadiene.*—The two possible stereoisomeric forms of *cyclo*pentadienebenzoquinone (cf. Alder and Stein, *Annalen*, **1933**, **501**, 247), the " endo- " and the " exo- " form, are shown in Fig. 1.* The possibility that the condensation product is a mixture of the two forms, which cannot be separated by crystallisation, is excluded by the experiments described on p. **1513**, which showed that under different conditions (concentration, temperature, solvent) the same product is invariably obtained, the purity of which is established by the melting point and by a sharp absorption band (maximum 2220 Å.). It is therefore certain that one of the isomerides predominates, and that no subsequent interconversion of the alternative products occurs.

Mutual orientations of the benzoquinone and *cyclo*pentadiene molecules suitable for 1 : 4-addition are represented in Figs. 2 and 3 of Part I (this vol., p. 833), and Figs. 2 and 3 of this paper depict their orientations subsequent to the regrouping of the electrons. These intermediate configurations are transformed into the stable *endo*- or *exo*-compound by a change in the direction of certain valencies.

Table I gives the dipole induction energies with which benzoquinone and *cyclo*pentadiene attract each other in the orientations corresponding to Figs. 2 and 3. For the calculation, the same assumptions were made as in Part I. As a measure for the separation of the reacting molecules, the atomic distance $B$IV (= $C$I) was again used and denoted by $d$.

Table I.

*Induction Energies corresponding to Different Intermediate Configurations in the* cyclo*Pentadiene–Benzoquinone Reaction.*

| | | | | |
|---|---|---|---|---|
| *endo*-Addition, intermediate configuration, Fig. 2 of Part I (cf. Fig. 2) | Distance $d$ (Å.) | 2·33 | 2·00 | 1·80 |
| | Induction energy (kg.-cals./mol.) | −3·3 | −6·7 | −9·6 |
| *exo*-Addition, intermediate configuration, Fig. 3 of Part I (cf. Fig. 3) | Distance $d$ (Å.) | 2·33 | 2·00 | 1·80 |
| | Induction energy (kg.-cals./mol.) | −2·5 | −4·0 | −5·3 |

The energies are greater in the mutual orientation suitable for the formation of the *endo*-isomeride; hence, it may be concluded that the activation energy of the *endo*-addition

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* It is not known whether the oxygen atoms are in the *cis*-position (as arbitrarily assumed in Fig. 1), in the *trans*-position, or coplanar with the carbon atom of the quinone ring. Perhaps there is an equilibrium between the different configurations.

($E_{\text{endo}}$) is smaller than that of the *exo*-addition ($E_{\text{exo}}$). As only one addition compound is found, this must be the *endo*-product.

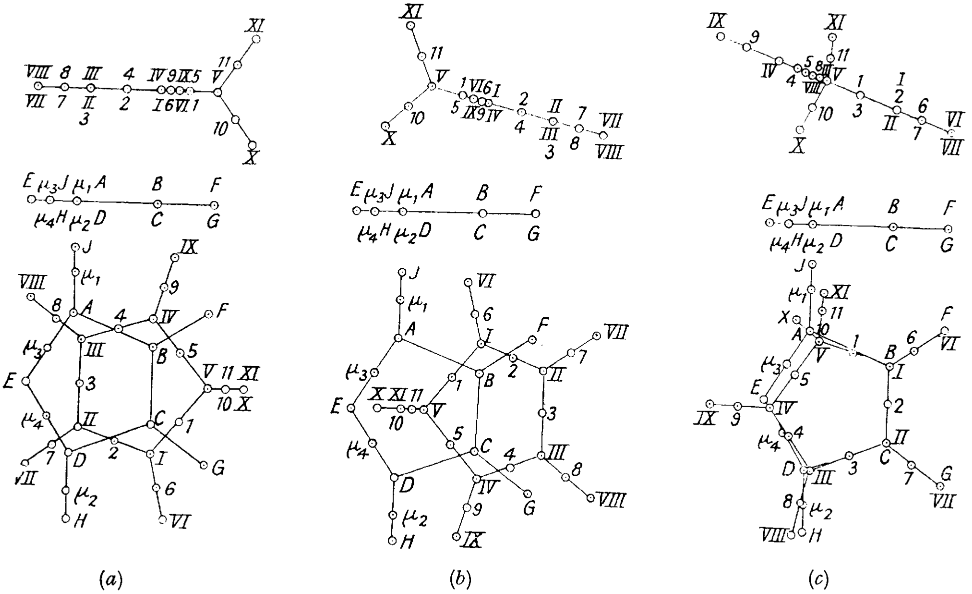
In the two equations $k_{\text{endo}} = Z_{\text{endo}}\, e^{-E_{\text{endo}}/RT}$ and $k_{\text{exo}} = Z_{\text{exo}}\, e^{-E_{\text{exo}}/RT}$, $Z_{\text{endo}}$ cannot be much smaller than $Z_{\text{exo}}$ because the statistical probability of the collided state is nearly the same for the two intermediate configurations (Figs. 2 and 3 of Part I). If it is assumed as a first approximation that the "dispersion forces" between the molecules in two orientations are equal,* the calculated difference in the induction energies may be taken as equal to $E_{\text{exo}} - E_{\text{endo}}$, and then for 20° the following ratios of the rate constants are obtained:

| | | | |
|---|---|---|---|
| Distance, $d$, in Å. ............... | 2·33 | 2·00 | 1·80 |
| $k_{\text{endo}} : k_{\text{exo}}$ ........................ | $\sim$6 | $\sim$100 | $\sim$1600 |

The difference in the rate constants, as estimated from the induction energy, is therefore sufficient to explain the steric selectivity provided that the distance $d$ does not much exceed 2Å.

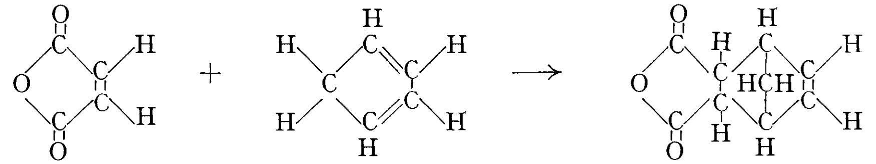
FIG. 4.

*Mutual orientations of maleic anhydride and* cyclo*pentadiene.*



(*a*) (*b*) (*c*)

*The Addition of Maleic Anhydride to* cyclo*Pentadiene.*—The formation of 3 : 6-*endo*-methylene-$\Delta^4$-tetrahydrophthalic anhydride from maleic anhydride and *cyclo*pentadiene was discovered by Diels and Alder (*Annalen*, 1928, **460**, 111; 1930, **478**, 137), and the steric



course of the reaction was elucidated by Alder and Stein (*Annalen*, 1933, **504**, 222; 1934, **514**, 1; *Angew. Chem.*, 1934, **47**, 837). In benzene solution only the *endo*-form of the addition product is formed. The *exo*-form has never been prepared directly from its components, but only indirectly from the *endo*-compound (Alder and Stein, *Annalen*, 1933, **504**, 247).

In Fig. 4 mutual orientations of *cyclo*pentadiene and maleic anhydride molecules are

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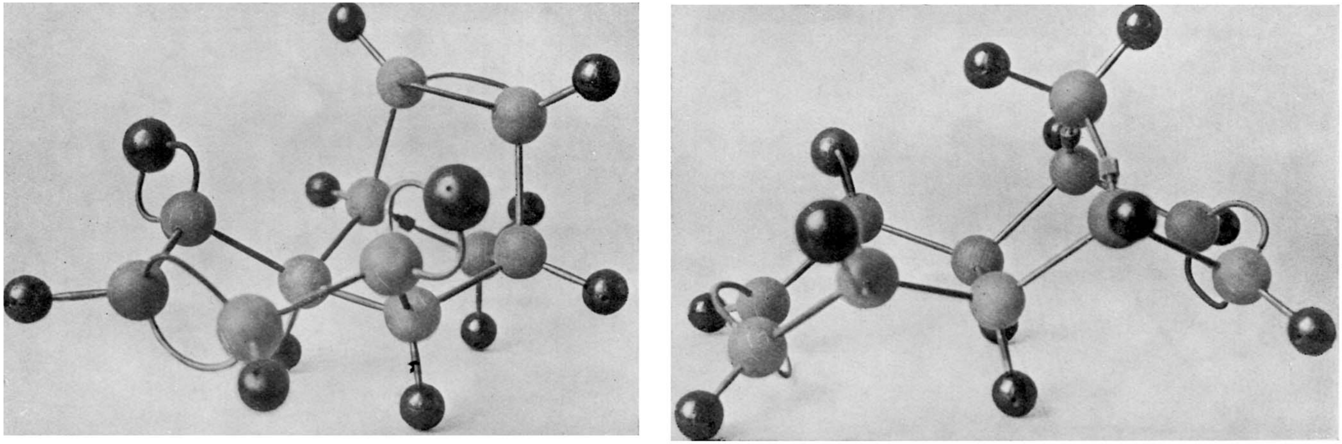
* See a following paper.

Fig. 1.

cyclo*Pentadienebenzoquinone.*



endo-*Form.*

exo-*Form.*

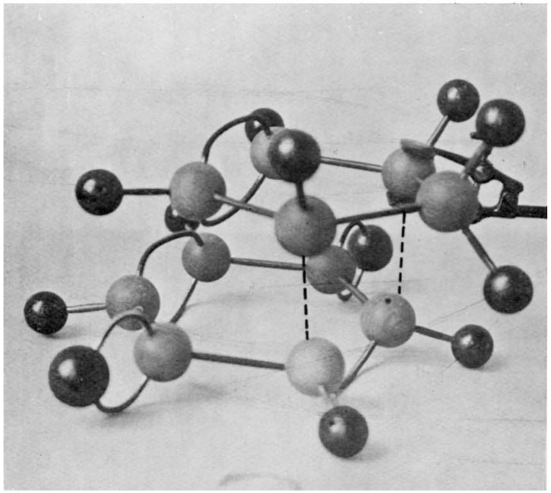


Fig. 2.

endo-cyclo*Pentadienebenzoquinone* (*intermediate configuration*).

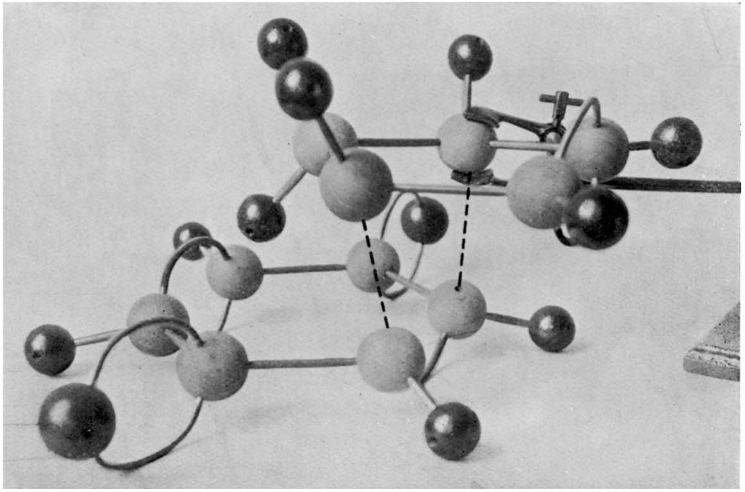


Fig. 3.

exo-cyclo*Pentadienebenzoquinone* (*intermediate configuration*).

[*To face p* 1512.

shown in plan and side elevation, the scale being correct for the lengths of the various bonds (cf. Part I, p. 832). It will be seen that orientation (*a*) would lead to the *endo*- and (*b*) to the *exo*-compound. For comparison, another orientation (*c*) corresponding to a hypothetical 1 : 2-addition product has been considered. In calculating the dipole induction energy (cf. Part I), the moment of the C = O bond ($\mu_1$, $\mu_2$) was taken as $2{\cdot}8 \times 10^{-18}$ and that of the C–O bond ($\mu_3$, $\mu_4$) as $1 \times 10^{-18}$ (cf. Wolf and Fuchs, Freudenberg's "Stereochemie," 1933, p. 263). The electric intensity due to $\mu_3$ and $\mu_4$ is given by

$$F_x = \frac{\mu_x}{r^3}(3\cos^2\delta - 1) + \frac{3\mu_y}{r^3}\sin\delta\cos\delta$$

$$F_y = \frac{3\mu_x}{r^3}\sin\delta\cos\delta + \frac{\mu_y}{r^3}(3\sin^2\delta - 1)$$

The *x* axis was chosen to pass through $\mu_3$ and $\mu_4$, $\mu_x$ and $\mu_y$ being the components of the moments in the direction of the *x* and the *y* axis respectively; *r* and $\delta$ have the same meaning as in equation (3) of Part I.

Although the small dipole moment experimentally observed for furan should not be regarded as evidence that the C–O moment therein is necessarily smaller than $1 \times 10^{-18}$ (Sutton, *Trans. Faraday Soc.*, 1934, **30**, 799), the possibility still exists that in maleic anhydride this moment is much smaller than $1 \times 10^{-18}$. In the last column of Table II the induction energy has therefore also been calculated upon the almost certainly incorrect assumption that $\mu_3$ and $\mu_4$ are zero. The distance *d* is that between the atoms *B*IV (= *C*I) and *B*I (= *C*II).

TABLE II.

*Induction Energies corresponding to Different Intermediate Configurations in the* cyclo*Pentadiene–Maleic Anhydride Reaction* (d = 2 Å.).

| | Intermediate configurations (Fig. 4). | Induction energy (kg.-cals./mol.). $\mu_3=\mu_4=1\times10^{-18}$. | $\mu_3=\mu_4=0$. |
|---|---|---|---|
| *endo*-Addition ............ | *a* | − 14·4 | − 8·4 |
| *exo*-Addition............... | *b* | − 9·2 | − 4·9 |
| 1 : 2-Addition ............ | *c* | − 7·2 | − 4·7 |

The energy with which the maleic anhydride and *cyclo*pentadiene molecules attract one another is at any rate greatest for orientation (*a*), whether $\mu_3$ and $\mu_4$ are zero or whether the C–O moment amounts to $1 \times 10^{-18}$. The activation energy must therefore be less for the *endo*-addition, and this product must be formed the more rapidly. This is in agreement with experiment. Upon the same assumption as on p. 1512 for 20°, the following ratios of the rate constants are obtained:

$\mu_3$ and $\mu_4 = 1 \times 10^{-18}$; $k_{\text{endo}} : k_{\text{exo}} = 7 \times 10^3$ ; $k_{\text{endo}} : k_{1:2\ \text{addn.}} = 2 \times 10^5$
$\mu_3$ and $\mu_4 = 0$ ; $k_{\text{endo}} : k_{\text{exo}} = 390$ ; $k_{\text{endo}} : k_{1:2\ \text{addn.}} = 550$

These values show that the experimentally observed steric selectivity and the preferential 1 : 4-addition as compared with the 1 : 2-addition can be regarded as dependent on the same cause.

## EXPERIMENTAL.

The ultra-violet absorption of *cyclo*pentadienebenzoquinone was determined by a method described elsewhere (Smakula and Wassermann, *Z. physikal. Chem.*, 1931, **115**, *A*, 353). The molar extinction coefficients are defined as in Part I, *viz.*, $\varepsilon = 1/cd. \log_{10} I_0/I$. The results were as follows:

| | mμ. | 200. | 204. | 208. | 212. | 216. | 220. | 224. | 228. | 232. | 236. | 240. | 244. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\varepsilon \times 10^{-3}$ l./g.-mol./cm. | *n*-Hexane | 6·1 | 4·6 | 5·7 | 7·8 | 10·9 | 12·2 | 11·7 | 8·5 | 6·3 | 4·8 | 2·8 | 1·3 |
| | Ethyl alcohol | | | 6·5 | 7·4 | 10·0 | 12·8 | 12·8 | 11·4 | 9·5 | 7·2 | 5·3 | 3·1 |

*cyclo*Pentadienebenzoquinone isolated from the five solvents mentioned in Table III at 20°, 40°, and 50°, was purified by recrystallisation from *n*-hexane, from which it separates in rectangular plates. All specimens had the same m. p., crystal shape, and colour. The yields at 40°

are shown in Table III. The product was weighed after one recrystallisation from hexane (m. p. 75—76°). In calculating the figures of the last column of Table III, allowance was made for the solubility in hexane. At 0°, 100 g. of the saturated solution contain 0·9 g. of *cyclo*pentadienebenzoquinone.

TABLE III.

*Isolation of* cyclo*pentadienebenzoquinone from various solvents at* 40°.

| Solvent. | Quinone, g. | *cyclo*-Pentadiene, g. | Vol., c.c. | Time, hrs. | Addition compd., g. |  | Addition compd. found, % of theor. |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  | weighed. | in soltn. (0°). |  |
| $C_6H_6$ * | 20 | 12 | 430 | 3 | 30 | 1·0 | 97 |
| EtOH * | 18 | 11 | 410 | 3 | 25·5 | 1·4 | 93 |
| $CCl_4$ | 24 | 15 | 390 | 8 | 36 | 2·1 | 98 |
| $n$-$C_6H_{14}$ | 11 | 7 | 370 | 6 | 17 | 0·5 | 97 |
| $CS_2$ | 6·2 | 10·1 | 320 | 20 | 15 | 0·7 | 96 |

* The experiments described in Table VIII of Part I were carried out under other conditions of concentration and temperature.

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