## II. POLYCYCLIC AND CAGE SYSTEMS OF CARBON COMPOUNDS.

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The chain of carbon atoms of a normal paraffin hydrocarbon is not straight, but at each carbon atom the line is bent so that compounds containing 5 or 6 carbon atoms readily form closed rings belonging to the isocyclic division of carbon compounds. Similarly, two polymethylene rings when condensed do not lie in the same plane, but form an angle with each other, and when sufficient cycloparaffin rings are present they give rise to a closed system of rings, termed by Beesley and Thorpe ${ }^{I}$ ' a cage.' In addition to such closed cages, other spatial arrangements occur, e.g., the compound $\mathrm{C}_{20} \mathrm{H}_{28}$ mentioned on p. 178. Probably the first representation of an isocyclic cage system was Ladenburg's prism formula for benzene, but the first compound to which a cage structure was definitely assigned is the substance represented by formula I and first prepared by Beesley and Thorpe. This triethyl ester was obtained by brominating the tribasic bicyclic acid, II, 1B-1:3, 1-methyl-cyclobutane-2:3:4-tricarboxylic acid, and pouring the product into alcohol.

1.

11.

The reaction consists in replacing the hydrogen atom attached to carbon atom No. 2 by bromine, the removal of the bromine attached to this atom with the hydrogen atom No. 4 and the formation of a new cyclopropane ring. At the same time the carboxylic groups are converted into COBr groups and finally, under the influence of the alcohol, into $\cdot \mathrm{CO} \cdot \mathrm{OEt}$ groups.

The acids III and IV which are stereoisomeric with No. II, and which differ only in the spatial arrangement of the hydrogen atoms and carboxyl groups attached to carbon atoms numbered 2 and 4 , do not yield a cage system under similar treatment.

[^0]
III.

IV.

The cause of the ready removal of hydrogen bromide and the closing of the ring is to be sought in the cis-positions of the hydrogen atoms in the acid II, i.e., in the cis-positions of the hydrogen and bromine after bromination.

Other compounds with cage structures had been previously prepared, although their cage structure had not been indicated at the time. Among these are the tricyclic compounds represented by formulae V to VIII:-
V. Semmler's tricyclene, ${ }^{1}$ 2B-1:3, methene-2:7:5,-3:4:4-trimethy1cyclohexane, from pinene dibromide, zinc dust and alcohol.
VI. Bredt and Savelsberg's ${ }^{2}$ 'Homocyclene,' 2B-I:3, dimethyl-methene-2:7:5,-2:3-dimethyl-cyclohexane, from camphor and fenchone by the aid of magnesium methyl iodide.
VII. Wagner and Brykner's isocyclene, ${ }^{3}$ 2B-I:3, methene-2:7:5, 4:4:5-trimethyl-cyclohexane.
VIII. Teresantalic acid. ${ }^{4}$

V.

VI.

VII.

VIII.

If it is assumed that all carbon atoms directly united are the same distance apart as stated by Ingold, ${ }^{5}$ then the compounds formed by bridging the cyclo-hexane ring as in formulae V to VIII will possess a cage type of structure.

[^1]When a simple cyclo-paraffin ring is bridged the whole of the carbon atoms constituting the original ring no longer lie in a single plane, i.e., the two smaller rings obtained by bridging the original large ring are not co-planar but form an angle with one another.

Practically all the systems dealt with in this paper are saturated cyclic, or rather polycyclic, systems and are derived from the cycloparaffins. In any particular cyclo-paraffin the hydrogen atoms do not all lie in one plane, but are symmetrically arranged in two planes one above the plane in which the carbon atoms constituting the ring are placed and the other below this. This arrangement gives rise to stereo-isomerism in the case of a disubstituted derivative, e.g., the well known cis-and trans-stereoisomerism of the cyclo-hexanedicarboxylic acids. The existence of the two planes of hydrogen atoms complicates the formation of bridges in cyclic paraffins. Thus in the case of a single bridge, whether a plain diagonal linkage or a bridging by means of one or two methene groups, the one hydrogen atom replaced may be in the cis-plane and the other in the trans-plane. Models show that a cis-cis-bridge, whether simple or containing several atoms, usually entails less strain in the molecule, and in the subsequent discussion it will be assumed that each individual bridge is a cis-cis-or trans-trans-bridge and not a cis-trans. In other words, the two hydrogen atoms in the ring replaced by the bridge always lie on the same side of the molecule.

When two bridges are present, then both bridges may be cis or one may be cis and the other trans, i.e., all four hydrogen atoms replaced may lie in the same plane or the two replaced by the one bridge may lie in a different plane from the two replaced by the second bridge.

It follows therefore that a compound such as that represented in Figure IX, which may be regarded as a derivative of cyclohexane with
IX. two meta bridges, can exist in two forms depending on whether the two bridges are cis or trans with respect to one another. Each form will consist of one fourmembered and two three-membered rings, but in (a) where the two linkings are cis the carbon atoms forming the apices of the two tri-rings lie on the same side of the plane of the tetra-ring and in (b) where the bridges are trans to one another the two apices lie on different sides of the tetra-ring.

a).

b).

In certain cases both forms, i.e., the doubly bridged cis-and the doubly bridged trans-form, appear to give equally stable systems and hence the number of possible compounds is increased. In other cases, e.g., two meta-and one para-bridge, the one form appears to be more stable than the others, as indicated by the strain entailed in forming models. In these cases only the more stable form is considered.

The difficulties engendered by the cis-and trans-arrangements of the hydrogen atoms when attempts are made to bridge a cyclic or polycyclic paraffin are well illustrated by the following examples.
(a) In attempting to form a $1: 4$-methene bridge in the compound, $\mathrm{CH}_{3}-\mathrm{CH}$

$\mathrm{CH}_{4}-\mathrm{CH}_{2}-\mathrm{OH}$, by the elimination of water, it is clear from what has been already stated that to obtain the bridging the H attached to carbon atom No. I and the $\mathrm{CH}_{2}-\mathrm{OH}$ group attached to carbon atom No. 4 must be cis with respect to each other. If they are trans then bridging will not take place.
(b) Somewhat more complex is the case represented by formula X
 where it is desired to form a plain metabridge by the elimination of water. Not only is it necessary that the OH attached to carbon atom No. 2 shall be in the cisposition with respect to the hydrogen atom attached to carbon atom No. 6, but it is also necessary that both this OH and H shall be trans with respect to the para bridge already present. ${ }^{\text { }}$

It is obvious that in most of these polycyclic compounds cis-transisomerism analogous to that occurring in the simple cycloparaffins will prevail when two substituents attached to two different methene groups are present.

[^2]Another interesting type of cis-trans-isomerism is met with when there is a bridge present and also a single substituent, e.g., methyl in one of the methene groups. Then the bridge may be either cis or trans to the methyl group. An example of such isomerism is to be found in the literature, viz., $1 B$-methene-1:7:3,-2:2:4-trimethylcyclohexane, ${ }^{1}$ XI.

XI.

XII.

Two isomeric compounds have been isolated and the isomerism is undoubtedly due to the relative positions of the methene bridge and the methyl group in the 4 -position. An analogous example is the corresponding $4-01,{ }^{2}$ XII.

The following pages give a classified list of a number of relatively simple isocyclic cage systems and closely related systems. In a number of cases their relationship to tetra-, penta-, and hexamethylene rings is indicated, e.g., the number and arrangement of the bridges.

The molecular formula is given in each case, also the number and types of unbridged rings forming the cage and finally the systematic name for each compound based on the principles detailed in Part I .

In the description of the types of rings constituting the cage or complex system it should be clearly understood that the carbon atoms constituting a ring do not necessarily all lie in the same plane, as they presumably do in the molecule of a simple cycloparaffin, and hence the stabilities of many of these rings cannot be compared with those of the corresponding cycloparaffins.

On plates IV-IX plane formulae for most of the compounds are given and these illustrate the system of numbering. On plates X and XI representations of the spatial models of some of the more interesting compounds are given.

[^3]A. Simple


1 Three-carbon ring. Two such rings parallel and joined by three pairs of carbon atoms

2 Four-carbon ring. Two parallel and joined by four pairs of carbon atoms.

3 : Four-carbon ring. Two parallel and joined by three pairs of carbon atoms.
B. Simple
$\mathrm{C}_{6} \mathrm{H}_{6}$
$\mathrm{C}_{8} \mathrm{H}_{8}$
$\mathrm{C}_{8} \mathrm{H}_{10}$
$\mathrm{C}_{8} \mathrm{H}_{12}$
$\mathrm{C}_{10} \mathrm{H}_{10}$
$\mathrm{C}_{12} \mathrm{H}_{12}$
$\mathrm{C}_{12} \mathrm{H}_{12}$
$\mathrm{C}_{12} \mathrm{H}_{20}$
$\mathrm{C}_{12} \mathrm{H}_{\mathrm{B}}$
$\mathrm{C}_{9} \mathrm{H}_{6}$
$\mathrm{C}_{12} \mathrm{H}_{6}$
$\mathrm{C}_{1 \mathrm{~s}} \mathrm{H}_{12}$
$\mathrm{C}_{18} \mathrm{H}_{2}$
$\mathrm{C}_{16} \mathrm{H}_{24}$

[^4]
## Cage Systems.

pyramidal forms.

| System of rings constituting cage |  | Systematic name |
| :---: | :---: | :---: |
| Four three-carbon rings | ... | 2B-1:3, 2:4,-cyclobutane. |
| Six three-carbon rings | ... | 4B-1:3, 1:4, 2:4, 2:5,-cyclopentane. |
| Four three-carbon rings ring. | four-ca | 3B-1:3, 1:4, 2:5,-cyclopentane. |
| Eight three-carbon rings | $\cdots$ | 6B-1:4, 1:5, 2:4, 2:6, 3:5, 3:6-cyclohexane. |

## prismatic forms

Two three-C-rings and three four-C-rings ${ }^{2} \ldots$

A cube of six four-C-rings.

Four four-C-rings and one six-C-ring

Two four-C-rings and two six-C-rings

Five four-C-rings at sides, top and bottom of two five-C-rings.

Sides of six four-C-rings, top and bottom two six-C-rings.

Sides of three six-C-rings, top and bottom two six-C-rings.

Sides of two eight-C-rings, top and bottom of two six-C-rings.

Ibid

Sides of six four-C-rings ; top and bottom of two three-C-rings.

Sides of eight four-C-rings and top and bottom of two four-C-rings.

Side of twelve four-C-rings and top and bottom of two six-C-rings.

Sides of six-C-rings ; top and bottom of two six-C-rings.

Top and bottom of two eight-C-rings and sides of four six-C-rings.

38-1:4, 2:6, 3:5-cyclohexane.

4B-1:6, 2:5, 3:8, 4:7,-cyclooctane.

38-1:4, 2:7, 3:6,-cyclooctane.

2B-methene-1:7:5, 2:8:4,-cyclohexane.

5B-1:7, 2:6, 3:10, 4:9, 5:8,-cyclodecane.

6B-1:8, 2:7, 3:12, 4:11, 5:10, 6:9,-cyclododecane.

38-4:9, methene-1:11:7, 2:12:6,-cyclodecane.

2B-dimetbene-1:9:10:6, 2:11:12:5,-cyclooctane.

2B-dimethine-1:9:9:10:6, 2:11:11:12:5,-cyclo-octa- $\Delta^{2: 4: 6: 8-\text { tetrene. }}$

6B-1:8, 2:5, 2:7, 3:7, 3:9, 4:6,-cyclononane.

8B-1:10, 2:7, 2:9, 3:6, 3:12, 4:9, 4:11, 5:8,-cycloतodecane.
$12 \mathrm{~B}-1: 14,2: 11,2: 13,3: 10,3: 18,4: 9,4: 17,5: 8$, 5:16, 6:13, 6:15, 7:12,-cyclooctadecane.
6B-2:11, $3: 8, \quad 4: 15, \quad 5: 12$, methene-1:17:13, 6:18:10,-cyclohexadecane.
4B-4:13, 6:11, methene 1:15:9, 2:16:8,-cyclotetradecane.
in making such cages with the aid of Engler's atom models.

## C. Two parallel rings joined by

| No. | Base | Formula |
| :---: | :---: | :---: |
| 1 | Two four-C-rings parallel and joined at two opposite corners by methene bridges. | $\mathrm{C}_{10} \mathrm{H}_{16}$ |
| 2 | Two four-C-rings joined directly at two opposite corners and by two methene bridges at remaining two. | $\mathrm{C}_{10} \mathrm{H}_{22}$ |
| 3 | Two four-C-rings parallel and joined by methene bridges at each corner. | $\mathrm{C}_{12} \mathrm{H}_{16}$ |
| 4 | Two six-C-rings parallel and joined by three methene bridges at three symmetrical positions. | $\mathrm{C}_{15} \mathrm{H}_{24}$ |
| 5 | Two six-C-rings parallel, joined directly at three alternate points and at remaining points by three methene groups. | $\mathrm{C}_{15} \mathrm{H}_{19}$ |
| 6 | Two six-C-rings parallel and joined at alternate points with three dimethene bridges. | $\mathrm{C}_{19} \mathrm{H}_{30}$ |
| 7 | Two six-C-rings parallel and joined at four symmetrical points by methene bridges. | $\mathrm{C}_{16} \mathrm{H}_{24}$ |
|  | D. Bridged hexar | ylene |
| 1 | Cyclohexare with two para bridges (trans.) ... ... | $\mathrm{C}_{6} \mathrm{H}_{3}$ |
| 2 | Cyclohexane with two para methene bridges (trans.) ... | $\mathrm{C}_{8} \mathrm{H}_{12}$ |
| 3 | Cyclohexane with two meta bridges (a) cis ... ... | $\mathrm{C}_{8} \mathrm{H}_{8}$ |
|  | Do. (b) trans ... ... | $\mathrm{C}_{8} \mathrm{H}_{8}$ |
| 4 | Cyclohexane with two meta methene bridges cis or trans ... | $\mathrm{C}_{8} \mathrm{H}_{12}$ |
| 5 | Cyclohexane with one meta and one para bridge (trans.) ... | $\mathrm{C}_{6} \mathrm{H}_{8}$ |
| 6 | Cyclohexane with one meta bridge and one para wethene bridge (trans.) | $\mathrm{C}_{7} \mathrm{H}_{10}$ |
| 7 | Cyclohexane with one meta methene and one para methene bridge (trans.) | $\mathrm{C}_{8} \mathrm{H}_{22}$ |
| 8 | Cyclohexane with one para and one methene para bridge (trans). | $\mathrm{C}_{7} \mathrm{H}_{10}$ |
| 9 | Cyclohexane with two meta bridges and one para bridge : the para trans to the two meta bridges. | $\mathrm{C}_{6} \mathrm{H}_{6}$ |
| 10 | Cyclohexane with two meta bridges and one para methene bridge trans to the two meta bridges. | $\mathrm{C}_{7} \mathrm{H}_{8}$ |

CAGF. Systems.-(contd.)
methene or polymethene bridges.

System of rings constituting cage
Systematic name

Two sides of eight-C-rings : top and bottom of two four-C-rings.

Top and bottom of two four-C-rings : sides of four five-C-rings.
Four sides of six-C-rings : top and bottom of two four-C-rings.

Three sides of eight-C-rings : top and bottom of two six-C-rings.

Sides of six five-C-rings : top and bottom of two six-C-rings.

Sides of three ten-C-rings : top and bottom of two six-C-rings.

Top and bottom of two eight-C-rings and sides of four six-C-rings. Identical with B 14.

## reduced napthalene rings.

System of four four-C-rings ... ...
System of four five-C-rings ... ...
One four-C-ring and base and two three-Crings on same side
Do. do. do. on opposite sides.
Base of one six-C-ring and ends of two fourC -atoms. Identical with B4.

Base of one three-C-ring sides of two fourC -and one five-C-rings.

Base of one three-C-ring, sides of three five-C-rings.

Base of one six-C-ring, sides of one four-Cand two five-C-rings.

Base of one four-C-ring, sides of one four-C-and two five-C-rings.

Identical with B 1

Base of one four-C-rings, sides of two five-C-rings and ends of two three-C-rings.

2B-methene-1:9:7, 3:10:5,-cyclooctane.

48-1:7, 2:6, 3:9, 4:8,-cyclodecane.

4B-1:8, 2:7, 4:11, 5:10,-cyclododecane.

3B-methene-1:13:7, 3:14:11, 5:15:9,-cyclododecane.

6B-1:12, 2:6, 3:14, 4:8, 7:11, 9:13,-cyclopentadecane.

3B-methene-3:17:13, 6:18:10, dimethene-1:15:16:8,-cyclotetradecane.

2B-1:4, 2:5,-cyclohexane.
2B-1:5, 3:7,-cyclooctane.
2B-1:5, 2:4,-cyclohexane.

2B-methene-1:7:5, 2:8:4,-cyclohexane.

2B-1:3, 2:5,-cyclobexane.
2B-1:3, methene-2:7:5,-cyclohexane.
2B-1:4, methene-2:8:6,-cycloheptane. ${ }^{1}$

2B-1:4, 2:6,-cycloheptane.

3B-1:4, 2:7, 3:5,-cycloheptane.

## D. Bridged hexamethylene and

| No. | Base | Formula |
| :---: | :---: | :---: |
| 11 | Cyclohexane with one para-bridge and two meta-methene bridge, cis to one another but irans to the para-bridge. | $\mathrm{C}_{8} \mathrm{H}_{10}$ |
| 12 | Cyclohexane with two meta-methene bridges (cis) and one para-methene bridge trans. | $\mathrm{C}_{9} \mathrm{H}_{12}$ |
| 13 | Cyclohexane with one para-bridge and two ortho-methene bridges. (a) All cis (b) ortho cis, and para trans, (c) one ortho and para cis and second ortho trans. | $\mathrm{C}_{8} \mathrm{H}_{10}$ |
| 14 | Cyclohexane with one dimethine bridge, each CH attached symmetrically to two ortho-C-atoms of the original ring. | $\mathrm{C}_{8} \mathrm{H}_{10}$ |
| 15 | One dimethine bridge as in D 14 but with an additional para-linking (trans.) | $\mathrm{C}_{8} \mathrm{H}_{8}$ |
| 16 | Cyclohexane with one dimethins bridge each CH . attached to two meta-C-atoms of ring. | $\mathrm{C}_{9} \mathrm{H}_{10}$ |
| 17 | Cyclohexane with one dimethine bridge as in D 16 and with a para-linking trans to the dimethine. | $\mathrm{C}_{8} \mathrm{H}_{8}$ |
| 18 | Cyclohexane with one dimethine bridge as in D 16 and a trans para-methene bridge. | $\mathrm{C}_{9} \mathrm{H}_{10}$ |
| 19 | Cyclohexane with two meta-dimethene bridges (cis) and one para-methene bridge (trans.) | $\mathrm{C}_{11} \mathrm{H}_{1}$ d |
| 20 | Cyclohexane with two ortho-dimethene bridges cis and one plain para bridge trans. | $\mathrm{C}_{10} \mathrm{H}_{14}$ |
| 21 | Cyclohexane with two ortho-dimethene bridges cis and one para-methene bridge trans. | $\mathrm{C}_{11} \mathrm{H}_{18}$ |
| 22 | Cyclohexane with two ortho-dimethene bridges cis and one para-dimethene bridge trans. | $\mathrm{C}_{22} \mathrm{H}_{2 \mathrm{~A}}$ |
| 23 | Cyclohexane with two meta-dimethene bridges cis and one para-dimethene bridge trans | $\mathrm{C}_{12} \mathrm{H}_{18}$ |
| 24 | Cyclohexane with a cyclobutane bridge, the four carbons of latter joined to carbons 1:2:4:5 of former. | $\mathrm{C}_{10} \mathrm{H}_{12}$ |
| 25 | Same as D 24 but joined to carbons 1:2:3:4. | $\mathrm{C}_{10} \mathrm{H}_{12}$ |
| 26 | Decahydronapthalene with plain para-linking in each ring (cis). | $\mathrm{C}_{10} \mathrm{H}_{14}$ |
| 27 | Same as D 26 but meta-linking (cis) in each ring in place of para. | $\mathrm{C}_{10} \mathrm{H}_{24}$ |

## Cage System-(contd.)

## reduced naphthalene rings-(contd.)

| System of rings constituting cage | Systematic name |
| :---: | :---: |
|  |  |
| Practically identical with B 3 ... ... | ...... |
| Base of one six-C-ring, sides of two five-Cring and ends of two four-C-rings. ${ }^{2}$ | 3B-1:5, 2:8, 4:7,-cyclononane. |
| One three-り-ring, two four-C-rings, one three-C-ring. | 3B-1:7, 2:6, 3:5,-cyclooctane. |
| Base of one six-C-ring, sides of two five-Crings and ends of two three-C-rings. | 38-1:5, 2:8, 4:6,-cyclooctane. |
| Bottom of two four-C-rings, ends of two three-C-rings and sides of two five-C-rings. | 4B-1:5, 2:8, 3:7, 4:6,-cyclooctane. |
| Base of one six-C-ring and sides of four four-C-rings. Practically identical with B3. | 3B-1:4, 2:7, 3:6,-cyclooctane. |
| Cube. Identical with B2 ... ... | ...... |
| Base of two four-C-rings, ends of two four-C-rings and sides of two five-C-rings. | 48-1:6, 2:5, 3:9, 4:7,-cyclononane. |
| Base of one eight-C-ring, ends and sides of four five-C-rings. | 3B-1:5, 2:9, 4:8,-cycloundecane. |
| Four four-C-rings ${ }^{2}$... ... ... | 3B-1:8, 2:7, 3:6,-cyclodecane. |
| Two four-C-rings and two five-C-rings ... | 3B-1:8, 3:6, methene-2:11:7,-cyclodecane. |
| Two four-C-rings and two six-C-rings ... | 3B-1:8, 3:6, dimethene-2:11:12:7,-cyclodecane. |
| Base of one eight-C-ring, sides of two six-Crings and ends of two five-C-rings. | 3B-1:6, 2:10, 5:9,-cyclododecane. |
| Base of one six-C-ring, top and sides of three four-C-rings and ends of two five-C-rings. | 48-1:6, 2:5, 3:9, 4:8,-cyclodecane. |
| Base of one six-C-ring, sides and ends of three four-C-rings and one six-C-ring, top of one four-C-ring. | 4B-1:6, 2:5, 3:8, 4:7,-cyclodecane. |
| Sytem of four four-C-rings same as D 20 ... | *.... |
| System of two three-C-rings and two five-C-rings. | 3B-1:9, 2:7, 3:5,-cyclodecane. |

${ }^{1}$ This is the same figure as C 2 less one $\mathrm{CH}_{2}$ group.

* This minus four hydrogen atoms gives B5.


## Classification of

D. Bridged hexamethylene and

| No. | Base | Formula |
| :---: | :---: | :---: |
| 28 | Same as D 27 but carbon atoms common to two original cyclo <br> hexane rings involved. | $\mathrm{C}_{10} \mathrm{H}_{14}$ |

Bridges between the two rings

| 29 | Decahydronaphthalene with bridges between carbon atoms | $\mathbf{C}_{\mathbf{1 0}} \mathrm{H}_{\mathbf{1 4}}$ |
| :--- | :--- | :--- |

Decahydronaphthalene with bridges between carbons Nos. 2 and 5,3 and 10 , and 4 and 7 of original rings.
E. Miscel

D 18 with two more methene bridges ; i.e., two six-C-rings parallel joined at 4 points, viz., i, 2, 4, 5 of lower with 1, 3, 4, 6 of upper and upper ring with a para dimethene bridge.
Same as D 29 but with plain para-bridge in each ring
Decahydronaphthalene with bridges between carbons Nos. 3 and 10, 4 and 7 of original rings.

Decahydronaphthalene with bridges between carbons Nos. 2 and 10,5 and 7 of original rings.

Decahydronaphthalene with bridges between carbons Nos.
2 and 5, 3 and 9,4 and 8 of original rings. carbons Nos. 1, 2, 4 and 5. carbons 1:3:5:8:10:12. ${ }^{2}$

$$
\mathrm{C}_{14} \mathrm{H}_{18}
$$

$$
\mathrm{C}_{9} \mathrm{H}_{12}
$$

$$
\mathrm{C}_{10} \mathrm{H}_{1,2}
$$ Cyclohexane with a: $\mathrm{CH} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}$ : bridge attached to

Same with an additional para methene bridge (trans)

Cyclohexane bridged at 6 points with a cyclotetradecane at
$\mathrm{C}_{10} \mathrm{H}_{10}$
$\mathrm{C}_{10} \mathrm{H}_{14}$
$\mathrm{C}_{10} \mathrm{H}_{14}$
$\mathrm{C}_{10} \mathrm{H}_{12}$

$$
\mathrm{C}_{20} \mathrm{H}_{28}
$$

Two diphenyl groups attached in $p p$-positions ... ...
$\mathrm{C}_{24} \mathrm{H}_{16}$ 3 and 9 and 4 and 8 of original molecule. ${ }^{1}$

[^5]Cage Systems-(contd.)

## reduced naphthalene vings-(contd.)

| System of rings constituting cage |  |  |  |  | Systematic name |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1bid | $\ldots$ | ... | ... | ... | 9,-cyclodecane. |

in the naphthalene molecule-
Base of one four-C-ring sides of two six-C- 3 3-1:7, 2:6, 4:8,-cyclodecaue. rings and ends of two five-C-rings.

Same as B 5 ... ... ...
Base of one six-C-ring, sides of two six-C. rings and ends of two four-C-rings.

Base of one eight-C-ring, sides of two six-Crings and ends of two three-C-rings.

Identical with D 24.

Identical with D 25.
3B-1:8, 2:5, 4:9,-cyclodecane

3B-1:6, 2:10, 5:7,-cyclodecane.

4B-1:9, 2:7, 3:12, methine-4:8:14:11,-cyclotridecane.

3B-2:8, 4:6, methene-1:9:5,-cyclooctane.

4B-1:5, 2:10, 3:7, 6:8, cyclodecane.

6B-2:7, 3:17, 4:15, 5:13, 6:10, methene-1:20:8,cyclononadecane.

4B-dimethine- 1:17:17:18:14, 2:19:19:20:5, 6:21:21:22:9, 10:23:23:24:13,-cyclohexadeca$\Delta$ 2:4:6:8:10:12:14:16-octene.

[^6]As already pointed out ${ }^{1}$ Beesley and Thorpe have prepared derivatives of the type $A_{1}$, and Semmler, Bredt and Savelsberg, Wagner and Brykners and others derivatives of type D6. Farmer ${ }^{2}$ has attempted to prepare compounds belonging to type $\mathrm{B}_{\mathrm{I}}$, and Turner ${ }^{3}$ has failed in preparing derivatives of type Bg.

In these laboratories experiments have been started with the object of preparing compounds belonging to the types B8, Bi4 and Dio.

For the compound B8 the following series of reactions are being studied.

## $\mathrm{NH}_{2} \cdot \mathrm{C}_{6} \mathrm{H}_{4}-\mathrm{C}_{6} \mathrm{H}_{5} \cdot \mathrm{NH}_{2} \longrightarrow \mathrm{OH} \cdot \mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{OH} \longrightarrow \mathrm{OH} . \mathrm{C}_{6} \mathrm{H}_{10} \cdot \mathrm{C}_{6} \mathrm{H}_{10} \cdot \mathrm{OH}$

Benzidine.

$$
\rightarrow \quad \mathrm{IC}_{6} \mathrm{H}_{10} \cdot \mathrm{C}_{6} \mathrm{H}_{10} \mathrm{I} \quad \rightarrow \quad \mathrm{C}_{6} \mathrm{H}_{10} \cdot \mathrm{C}_{6} \mathrm{H}_{10}
$$

For a compound belonging to type Bi4, the reactions under examination are the elimination of hydrogen chloride from the acid chloride of anthraquinone-2:6-dicarboxylic acid or of water from the corresponding acid.

The method adopted for preparing a compound derived from the parent substance, type Dro, is the elimination of water from the ditertiary alcohol, ${ }^{4}$ i:2-dimethylcamphan-1:2-diol., obtained by condensing camphor-quinone with magnesium methyl iodide.

In conclusion we wish to thank Dr. H. E. Watson for many valuable suggestions.

[^7][^8]
## PLATE V.



B 3.


B 10.


BII.


B12.



B14.


## PLATE VI.



C 2.


D3.

PLATE VII.


## PLATE VIII.



D 20.

021.


D 22 .


D 28 .


032.


EI.


E2.


E3.



## PLATE X.


D 5 .

07.

08.

010.


D 11.

PLATE XI.

019.


D 29 .


D31.


EI.


E 4.


[^0]:    ${ }^{1}$ J. Chern. Soc., 1920, 117, 617.

[^1]:    ${ }^{1}$ Ber., 1902, 35, 1018.
    ${ }^{3}$ J. Russ. Phys. Chem. Soc., 1903, 35, 536.
    3 J. Chem. Soc., 1920, 117, 607.
    ${ }^{2}$ J. Pr. Chem., 1918, [ii], 98, 99.

    - Semmler, Ber, 1911, 44, 463.

[^2]:    ${ }^{1}$ Another example of this type is seen in the elimination of hydrogen bromide from one only of the three stereoisomeric acids mentioned by Beesley and Thorpe, loc. cit.

[^3]:    ${ }^{1}$ Nametkin, J. Russ. Phys. Chem. Soc., 1922, 54, 177.
    ${ }^{2}$ Lipp, Ber., 1923, 56B, 2101.

[^4]:    ${ }_{2}^{1}$ Nos. A 2, A 3 and A 4 are highly improbable forms, as indicated by the strain entailed
    ${ }^{2}$ Similar to Ladenburg's prism formula for benzene.

[^5]:    ${ }^{1}$ These figures refer to the numbers of the carbon atoms in the
    ${ }^{2}$ May be regarded as an acenaphthene type of compound derived

[^6]:    naphthalene ring starting with one of the quaternary carbons as No. 1. from anthracene perhydride.

[^7]:    ${ }^{2}$ P. 166.
    ${ }^{3}$ Ibid., 1915, 107, 1495.

[^8]:    ${ }^{2}$ Ibid., 1923, 123, 3332.

    * Forster, J. Chem. Soc., 1905, 87, 141.

