Syntheses of the hydroaromatic series;
by Otto Diels and Kurt Alder.

(Received 13-Dec-1927)

In one study, W. Albrecht has observed and reported the formation of cyclopentadienequinone by the addition of cyclopentadiene to $p$-quinone. He labeled the resulting compounds as both "cyclopentadienequinone" and "di-cyclopentadiene quinone" as produced from compounds I and II:

![Chemical structures](https://www.mjphd.net/images/structures.png)

He therefore implies that cyclopentadiene attaches to the double bonds of the quinone with its methylene group and that the reaction product contains both double bonds of cyclopentadiene.

H. Staudinger on the other hand tends toward the view that quinone and cyclopentadiene assemble to form cyclo-butane derivatives, as is also assumed to happen in the polymerization of cyclopentadiene to di-cyclopentadiene. He therefore prefers the "cyclopentadiene quinone", which is Albrechts structural formula III.

The results reported in the experiments hereafter leave no doubt that both views are wrong.

Work from O. Diels, J.H. Blom and W. Koll provided reliable evidence that cyclopentadiene had an equivalent structure to a semi-quinone azo ester to produce N,N'-Dicarboxäthyl-endomethylene tetrahydropyridazine (IV), ie incorporating the addition of a methylene bridge:

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gives a very different picture of the way in which the cyclopentadiene can be incorporated.

Also H. Euler and Josephson, who deal with the reaction of isoprene with quinone using 2 moles of the hydrocarbon to 1 mol of quinone have observed what they believe is the joining at the 1,4 position and therefore they state the reaction product to have the formula of $V^*$.  

As much is already obvious from earlier observations but strangely it was not contested by W. Albrecht in his discussion of the notion of the "cyclopentadiene quinone" and the "di-cyclopentadiene quinone" as "endo-methylene" where he concludes that structures $VI$ and $VII$ are highly probable:

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We used the two compounds in further experiments, which along with other observations made by us demonstrated the correctness of this view.

"Cyclopentadienequinone" appears then as an endomethylene derivative of hydrogenated $\alpha$-naphthoquinone and "di-cyclopentadiene quinone" as a descendant of a hydrogenated anthraquinone and here the 2 methylene bridges are incorporated.
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*The authors point out that the correct position of the methyl groups is still undetermined.
Upon reduction using zinc powder and acetic acid Albrecht has found that "cyclopentadiene quinone" accepts 2 atoms of hydrogen. Albrecht gives formula VIII for the hydrogenation product, but by our intuition we regard IX as the correct structure:

Catalytic hydrogenation of IX and quenches the second double bond and (X) is formed. Replacement of its two oxygen atoms by hydrogen using a Clemmensen reduction leads to endomethylene 1,4-decalin (XI). The formation of an unsaturated hydrocarbon by Clemmensen reduction was to be expected and was probably achieved by elimination of water from a di-ol intermediate.

With the formation of C_{11}H_{18} (compound XI) the reduction of Albrecht's "Cyclopentadienquinones" has reached its end.  

Its discoverer claims—although with reservations—to have a structure matching that of I. If this were true then a complete hydrogenation would result in a hydrocarbon of C_{11}H_{20}.

*The conditions for reduction of VI and VII and other similar oxygen-containing products shall be reported later.
Even Albrecht’s "di-cyclopentadienequinone" (see. Formulas II and VII) has been shown by O. Diels, J.H. Blom and W. Koll by hydrogenation experiments to be a tetra-hydro compound (XII) and it is confidently anticipated that both double bonds are in the position shown in formula VII. The two carbonyl oxygen atoms do not resist Clemmensen reduction and can be replaced by hydrogens, recovering the di-endomethylene (1.4—5.8)-tetradecahydroanthracen (XIII), which upon dehydrogenation with selenium yields 6 atoms of hydrogen so that an Octo-hydroanthracene with two methylene bridges most likely arises with the structure XIV:

![Formula XIII](image1)

All these observations can not be reconciled with the view Albrecht and they are in fact in total disagreement; but they alone are still do not provide strong enough evidence to prove the correctness of the structural formulas we represent.

More definitive proof follows from the observations of many others that we have read in the literature.

Firstly, it has been seen that the addition of 1 mol of butadiene to 1 mol of α-naphthoquinone succeeds with the utmost ease.

The reaction product (XV) can on the one hand accept hydrogen, but on the other hand it is also smoothly oxidized to anthraquinone:

![Formula XV](image2)

This result is, in addition to its value as evidence in this matter, of practical importance because it shows a convenient way to obtain partially hydrogenated anthraquinones.

Further evidence is provided by considering the following examples.

Given that azo esters behave similarity upon exposure to quinones as do cyclopentadienes and other hydrocarbons, it seemed possible that the latter would unite with the anhydrides of maleic, citraconic and itaconic to give stable compounds. Because the analogous series in these systems, a trend can be seen to emerge when assembling their formulas:
this is deepened by the observation of P. Pfeiffer and Th. Böttler who attribute the habit of colour formation that occurs when maleic anhydride is exposed to aromatic hydrocarbons, amines, phenols and other compounds in solution to the formation of a quinhydro complexation species (Translator’s note: original text calls the species “chinhydroartigen”).

We have now found that maleic anhydride, as well as the free maleic acid, and also citraconic and itaconic anhydride—usually at ordinary temperatures—attach readily to cyclopentadiene and butadiene, but also to more complex hydrocarbons having a system of conjugated double bonds such as attack cyclo-hexadiene or phellandrene in the same manner as do azo esters and quinones. The double bond of said unsaturated acids or anhydrides opens and in all cases annexes with the free valences in the 1,4 position of the hydrocarbons in question, with the new double bond formed between carbon atoms 2 and 3.

The resulting products are not numerous "molecular compounds", but are well knit and stable. Some of them can be identified by conversion into familiar substances.

The reaction of maleic anhydride with cyclopentadiene gave a quantitative yield of endomethylene-3,6-tetrahydro-Δ^4-0-phthalic anhydride (XVI).

The free acid, which forms during the brief heating of the anhydride with water, catalytically takes hydrogen 2 atoms and transforms into the cis-3,6-endomethylene-hexahydro-0-phthalic acid (XVII). In an analogous way to the Baeyer cis-hexahydro-0-phthalic acid and also the "Endomethyleneic acid" easily can rearrange into the corresponding trans compound.

The anhydrides of citraconic acid and itaconic acid (XVIII) react equally easily with cyclopentadiene to successfully formed the analogous compounds.
Of great interest also is that 1,2-dihydrobenzene (cyclohexadiene) connects in the same way with maleic anhydride. The resulting product in this case (XIX) is characterized by a two limbed bridge and should be of interest in the researches of steric relationships. According to O. Ashan and E. Mohr the ring-system may be regarded as unstrained (XIXa).

It also works with hydrocarbons that have a more complicated structure—provided that they contain only the characteristic grouping of double bonds—it was unexpected how extraordinarily smooth the reaction occurred to give the target compound as demonstrated by the exposure of maleic anhydride to α-phellandrene. The two compounds react with one another even at room temperature, and in this case produce a product that is characterized by a two-membered bridge (XX).

The simplest hydrocarbon with a system of conjugated double bonds, butadiene, has a reactive ability corresponding to cyclopentadiene and the other mentioned hydrocarbons.

It reacts with maleic anhydride to form tetrahydro-Δ⁴-o-phthalic acid anhydride (XXI):

In hot water the free cis-tetrahydro-Δ⁴-o-phthalic acid is transformed. The anhydride prepared by us shows a significant difference in melting point with that from the preparations described by Baeyer. What this is based upon we are at present unable to say, but we shall make every effort to determine the cause. Since the tetrahydro acid, as shown by us, undergoes ready hydrogenation and as also identified by us undergoes and addition reaction with the cis-hexahydro-o-phthalic acid, and it can also rearrange flawlessly to the equally well-known trans-acid and several derivatives, we must assume that our anhydride is derived from the cis-tetrahydro-Δ⁴-o-phthalic acid.

Of emerging interest is the further conversion of anhydrides of maleic acid and other unsaturated acids mentioned to hydro-aromatic compounds but those that have ring systems with impeding carboxyls are expected to give significant difficulties in this approach.
Therefore the experimental question posed by us was whether the principle found by us could possibly be used to prepare monobasic acids, or of even more convenience aldehydes.

The reactions carried out with this in mind have led to a great success.

Any acrylic acid such as acrolein can be in the most convenient way used to prepare cyclopentadiene in a few minutes in a theoretical yield such as endomethylene-2,5-tetra-hydro-Δ^3-benzaldehyde (XXII):

\[
\begin{align*}
\text{OHC–CH} & \quad \text{CH}_2 \quad \text{CH} \\
\text{CH}_2 & \quad \text{OHC–CH} \quad \text{CH} \\
\text{CH} & \quad \text{CH}_2
\end{align*}
\]

2 atoms of hydrogen are gobbled up by the hydrogenation and the endomethylene 2,5-hexahydro-benzaldehyde (XXIII) is furnished.

When cyclopentadiene is replaced by butadiene in this reaction, it first converts to Δ^3-tetrahydrobenzaldehyde* whose semicarbazone can easily be hydrogenated to the corresponding derivatives of hexahydro-benzaldehyde. This fact can be demonstrated by the cleavage of the semicarbazone.

All the information supplied in the previous observations and results suggests that there is no longer any doubt about the way in which the addition reaction occurs of hydrocarbons with the appropriate conjugated double bond systems.

Beyond that the results of our study are not only of interest in elucidating the theoretical matter of the role that valence electron ratios in polycyclic systems play, but what may be of even more importance in practical terms is the implication of these valence ratios on the preparation of valuable compounds. It seems to us that the possibility of synthetic preparation of the more complicated natural products related to or identical compounds can be brought into closer view such as terpenes, sesquiterpenes, or perhaps even alkaloids #.

We explicitly reserve the right to solve the problems of the application of the reactions here described that were found by us.

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*This aldehyde has already been achieved by W. Sobecki after a laborious process.

# Necessary for us to make this assertion was our observation that even pyrrole and N-methylpyrrole react with maleic anhydride. These results will form the subject of a subsequent communication.
Our observations seem important to us in biological terms. We feel that it is quite likely that the formation of terpenes and other natural products proceeds in nature in this same way as has been shown to us by a large number of examples, such as that from Wallach whose experiments have delivered the preparation of dipentene from isoprene:

This general trend will be applicable elsewhere with appropriate compounds.

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Also the I. G. Farbenindustrie-Aktiengesellschaft-Leverkusen we thank you for your committed promotion of our preparative investigations by the granting a funds.
Similarly, we thank Haarmann and Reimer (Holzminden) and Schimmel & Co (Leipzig) to whom we are indebted for the supply of terpenes for preparations.

Experimental section

Although they were not included in the original text, images and IUPAC names of the numbered compounds have been added by Matthew to the experimental section for the convenience of researchers.

*Endomethylene-1,4-dioxo-5,8-decahydronaphthalene (X).*

IUPAC: Tricyclo[6.1.1.0\(^2,7\)]undecane-3,6-dione

The start material had been previously shown by W. Albrecht to have a m.p of 34–35 °C. 30 g were dissolved into 150 mL alcohol and then treated with 0.4–0.5 g of colloidal
palladium and using the Skit-Frankschen apparatus exposed to hydrogen at 1 atm. The flask was shaken at increased pressure and the calculated amount of hydrogen is taken up and the reaction carried out in about 30 min. After distilling off the alcohol in vacuo the residue solidifies on cooling to a crystalline mass. To remove the catalytic substances the product is dissolved in diethyl ether and the flocculated palladium filtered off from the solution. Slow evaporation of the ether gives the reaction product splendidly formed pure white crystals. For analysis the compound was recrystallized from boiling petroleum ether and dried over phosphorus pentoxide under vacuum at room temperature.

**5.300 mg Compound: 14.380 mg CO₂, 3.81 mg H₂O.**

<table>
<thead>
<tr>
<th>C₁₁H₁₄O₂</th>
<th>Calculated: C 74.2  H 7.9</th>
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<tr>
<td>Found:</td>
<td>C 74.0  H 8.0</td>
</tr>
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</table>

The compound was obtained in close to quantitative yield, m.p. 56–57 °C. Readily soluble in alcohol and ether, barely soluble in cold petroleum ether or cold ligroin.

**Dioxim:** 5 g of the dioxo-compound (dicarbonyl compound) were dissolved in a little alcohol and added to a solution of 5 g hydroxylamine hydrochloride and 10 g of sodium acetate, then the dioxime precipitates in a few moments as a dense, flakey crystalline mass. It was filtered, meticulously washed with water and recrystallized from boiling alcohol. M.p. 217–218 °C.

*Endomethylene-1,4-decalene (XI).*

![XI](image)

IUPAC: Tricyclo[6.1.1.0²⁷]undecane

A solution of 30 g of the compound described in the previous section in 100 mL of glacial acetic acid was kept cold while 250 g of amalgamated zinc dust was added, followed by 300 mL of raw, fuming hydrochloric acid. The reaction mass was then refluxed for 4–5 hours; at the beginning of the operation the occurrence of oil droplets in the condenser indicated the start of the reduction. As the reaction proceeded, two more 100 mL aliquots of hydrochloric acid were added. On completion of the reduction the hydrocarbon was distilled using a descending condenser. The distillate was worked up by extraction with into diethyl ether, washing the ether solution with bicarbonate, drying with sodium sulfate and then evaporation of the ether and vacuum distillation of the residue. The yield of the hydrocarbon is about 15 g. It presents as a water-clear, mobile liquid with a characteristic terpene odour and has a boiling point of 84–85 °C at 15 mmHg, or 91 °C at 22 mmHg.

For analysis, the material was distilled twice over sodium under reduced pressure.
5.107 mg Compound: 16.630 mg CO₂, 5.12 mg H₂O. — 5.440 mg Compound: 17.710 mg CO₂, 5.47 mg H₂O.

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<tr>
<td>C₁₁H₁₈</td>
<td>C 88.0</td>
<td>C 88.6, 88.83</td>
</tr>
<tr>
<td>C₁₁H₁₈</td>
<td>H 12.0</td>
<td>H 11.22, 11.25</td>
</tr>
</tbody>
</table>

Molecular weight determination: 0.3353 g compound: 16.40 g Benzene, Δ = 0.700°.

**Di-(endomethylene)-1,4-5,8-tetradecahydroanthracene (XIII).**

IUPAC: Pentacyclo[10.2.1.1⁵,8.0²,11.0⁴,9]hexadecane

A solution of tetrahydro-dicyclopentadienequinone (25 g) in 300 mL of glacial acetic acid was mixed with 300 mL of crude fuming hydrochloric acid. 200 g of amalgamated zinc dust was then added and the reaction mass heated at reflux for 4–5 hours, at which time a further 200 mL aliquot of hydrochloric acid was added and the reflux continued for a further 2 hours. After cooling, both the unreacted zinc slurry and the acid solution were extracted several times into diethyl ether. After washing the ether solution with bicarbonate and drying with sodium sulfate, the ether was evaporated off. The unremovable residue that remained behind in the flask was treated with vacuum fractionation to provide about 8 grams of water-clear distillate, which came over at 155–150 °C under pressure of 15 mmHg to give a virtually pure hydrocarbon product. For complete purification the product could be vacuum distilled 2–3 times from a flask containing sodium.

The hydrocarbon thus obtained presents as a water-clear, viscous oil that distills at 157–159 °C under pressure of 16 mmHg. It has a characteristic terpene-like odor and is insoluble in water, alcohol and glacial acetic acid; slightly soluble in ether.

0.1241, 0.1742, 0.1849, 0.1970 g Compound: 0.4017, 0.5686, 0.6036, 0.6419 g CO₂, 0.1174, 0.1657, 0.1736, 0.1865 g H₂O.

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<tr>
<th>Compound</th>
<th>Calculated</th>
<th>Found</th>
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<tbody>
<tr>
<td>C₁₆H₂₂*</td>
<td>M 214</td>
<td>M 214, 214</td>
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</table>

* It is possible that this hydrocarbon is mixed with a small amount of the unsaturated compound C₁₆H₂₂.
Di-(endomethylene)-1,4,8-octohydroanthracene (XIV).

IUPAC: Pentacyclo[10.2.1.1^5,8.0^2,11.0^4,9]hexadeca-2,4(9),10-triene

10 g of the hydrocarbon described in the previous section were placed in a quartz vessel with 5 g of metallic selenium and heated at 360–380 °C for 8–10 hours. During this time copious amounts hydrogen selenide were evolved. After cooling, the reaction mass was extracted into diethyl ether, the unchanged selenium was filtered from the ether solution, the ether was then removed by evaporation and the oil residue was purified by fractional distillation.

The first fraction (150–170 °C, 15 mmHg, I) was a solid component that contained some unreacted start material, whereas the higher boiling fraction (170–190 °C, II) was a lightly colored oil of high viscosity, which upon cooling solidified into a glassy mass.

Fraction I gave a white crystalline powder when the oily fractions were pressed into clay. For Fraction II would give a second portion of these crystals when rubbed with a little alcohol after standing in the cold.

The crude product can be purified by a single recrystallization from alcohol that gives a pure white, beautifully crystalline product that melts at 157 °C and is readily soluble in the common organic solvents even at low temperatures.

For analysis it was recrystallized a second time from alcohol and dried under vacuum over phosphorus pentoxide at 56 °C.

5.069 mg Compound: 16.980 mg CO₂, 3.96 mg H₂O.

\[
\begin{array}{c|c|c}
\text{C}_{16}\text{H}_{18} & \text{Calculated:} & \text{C 91.4} & \text{H 8.6} \\
& \text{Found:} & \text{C 91.4} & \text{H 8.7} \\
\end{array}
\]

\(\Delta^2\text{-Tetrahydroanthraquinone (XV).}\)

IUPAC: 1,4,4a,9,9a,10-Hexahydroanthracene-9,10-dione
A suspension of 12 g α-naphthoquinone in 15 mL of alcohol was heated with 4–5 g of butadiene in a sealed tube for 3 hours at ~ 100 °C. After cooling the content of the tube solidified into a magnificent mass of crystals, which were coloured brown by a minor contaminant. The crude product can be easily cleaned by repeated recrystallization from alcohol or middle-boiling ligroins and passing through a little charcoal allows it to form beautiful white crystals, m.p. 102–103 °C.

**4.417 mg Compound: 12.835 mg CO₂, 2.38 mg H₂O. — 5.168 mg Compound: 15.015 mg CO₂, 2.72 mg H₂O.**

<table>
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<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₄H₁₂O₂</td>
<td>C 79.24</td>
<td>C 79.26, 79.27</td>
</tr>
<tr>
<td></td>
<td>H 5.66</td>
<td>H 6.03, 5.88</td>
</tr>
</tbody>
</table>

In the common solvents the compound dissolves easily even in the cold, but more readily still in heated solvents. It discolored a solution of permanganate in acetone instantly.

*Oxidation of Δ²-Tetrahydroanthraquinone (XV) to anthraquinone.*

If 0.5 g of the hydrogenated compound is dissolved in glacial acetic acid and ~ 3 times the stoichiometric amount of chromium trioxide is added and the mixture heated to boiling, a fairly instant reaction occurs with vigorous foaming. After the reaction is completed the mass is poured into ice water and the anthraquinone product instantly precipitates out. After recrystallization from glacial acetic acid, it shows the correct melting point as was identified by a composite sample of the Oxa-anthrano compound provided by Liebermann.

*cis-Endomethylene-3,6-Δ⁴-tetrahydrophthalic acid anhydride (XVI).*

IUPAC: 4-Oxatricyclo[5.2.1.0²⁶]dec-8-ene-3,5-dione
To a suspension of 1 mol of maleic anhydride in 5 times the amount of benzene, 1 mol of cyclopentadiene was gradually added with constant cooling—the components react too quickly with excessive heat. The maleic anhydride was dissolved but quickly during the process the anhydride of the new acid separates out as snow-white, glossy crystals. The yield is almost quantitative.

The compound is only sparingly soluble in the usual solvents and after two recrystallizations from boiling ligroin gives a m.p. of 164–165 °C. For analysis it was dried in vacuo over phosphorus pentoxide at 56 °C.

**5.189 mg Compound: 12.590 mg CO₂, 2.35 mg H₂O.**

\[
\begin{align*}
\text{C}_9\text{H}_8\text{O}_3 & \quad \text{Calculated:} & \text{C} & \text{65.85} & \text{H} & \text{4.88} \\
\text{Found:} & \quad \text{C} & \text{66.19} & \text{H} & \text{5.07}
\end{align*}
\]

*cis-Endomethylene-3,6-Δ⁴-tetrahydropthalic acid.*

If the anhydride described in the previous section is boiled for a short time in water it gradually goes into solution, and upon cooling, the free acid precipitates as white crystals. It melts after repeated recrystallization from boiling water at 177–179 °C, but the melting temperature depends a lot on the way the heating is done.

For analysis the compound was dried in vacuo over phosphorus pentoxide.

**4.808 mg Compound: 10.450 mg CO₂, 2.47 mg H₂O.**

\[
\begin{align*}
\text{C}_9\text{H}_{10}\text{O}_4 & \quad \text{Calculated:} & \text{C} & \text{59.3} & \text{H} & \text{5.5} \\
\text{Found:} & \quad \text{C} & \text{59.3} & \text{H} & \text{5.7}
\end{align*}
\]

Permanganate in soda and hydrobromic acid act immediately on the acid.
English translation of Diels-Alder 1928 paper in Justus Leibigs Annalen der Chemie

cis-Endomethylene-3,6-hexahydrophthalic acid (XVII).

IUPAC: Bicyclo[2.2.1]heptane-2,3-dicarboxylic acid

A suspension of 10 g of the unsaturated acid just described was exposed to with pure sodium until the initially precipitated sodium salt went back into solution. The solution was then treated with 0.2 g of palladium colloid at room temperature and then the flask filled with hydrogen to 1 Atm and shaken. In a few minutes the hydrogen uptake had ceased and equally that calculated for one double bond. On acidification the new acid separated out as shiny crystals, which after two recrystallizations from boiling water had a m.p. of 160–161 °C.

4.222 mg Compound: 11.185 mg CO₂, 3.19 mg H₂O.

| C₉H₁₂O₄ | Calculated: C 58.70 | H 6.52 |
| Found: C 58.43 | H 6.84 |

The new compound is stable against sodium permanganate and hydrobromic acid.

Anhydride compound: The acid is treated with acetyl chloride to give the anhydride that has a m.p. of 167–168 °C.

4.893 mg Compound: 11.690 mg CO₂, 2.80 mg H₂O.

| C₉H₁₀O₃ | Calculated: C 65.06 | H 6.02 |
| Found: C 65.18 | H 6.40 |

Rearrangement of the cis and trans acid.

3 g of the cis-acid were placed with 10 mL of fuming hydrochloric acid (spec. weight 1.19) and heated to 180–190 °C in a sealed tube for 2-3 hours. After cooling the tube’s contents gave well-developed crystals, which after two recrystallizations from boiling water melted at 194–195 °C and presented as the trans form of endomethylenehexahydrophthalic acid.

The trans-acid is easily soluble in hot water; moderately soluble in cold water and most organic solvents.
5.174 mg Compound: 11.150 mg CO₂, 3.10 mg H₂O.

C₉H₁₂O₄  Calculated:  C 58.7 H 6.5
Found: C 58.8 H 6.7

cis-Δ⁴-Tetrahydrophthalic acid (XXI) from butadiene and maleic acid anhydride.

IUPAC: 1,3,3a,4,7,7a-Hexahydro-2-benzofuran-1,3-dione

2–2.5 g of butadiene were dissolved in 10 mL of benzene and 4 g of maleic anhydride was then added and the mixture left in a sealed tube for 12 hours, it was then heated to 100 °C for 5 hours using a water bath. After cooling, the tube content consisted of a snow-white crystalline mass. This was suction filtered and purified, and the thus obtained anhydride of tetrahydrophthalic acid further purified by repeated recrystallization from hot middle-boiling ligroin. The yield was quantitative.

4.739 mg Compound: 11.010, 11.870 mg CO₂, 2.36, 2.50 mg H₂O.

C₈H₈O₃  Calculated:  C 63.2 H 5.3
Found: C 63.4, 63.3 H 5.6, 5.5

The compound melts at 103–104 °C. It is readily soluble in the common organic solvents; slightly soluble in cold petroleum ether and ligroin. If it is boiled with water it dissolves after a short time and upon cooling the cis-Δ⁴-tetrahydrophthalic acid separates out as a shiny white crystalline mass, which after another recrystallization from water gives a m.p. of 166 °C.

4.600 mg Compound: 9.550 mg CO₂, 2.38 mg H₂O.

C₈H₁₀O₄  Calculated:  C 56.5 H 5.9
Found: C 56.6 H 5.8

cis-Hexahydrophthalic acid.

To a suspension of cis-Δ⁴-tetrahydrophthalic, sodium hydroxide crystals were added until everything dissolved. The solution was boiled briefly, treated with palladium/barium sulfate and shaken in a hydrogen atmosphere. The reduction was smooth, although not overly fast. After several hours, the calculated amount of hydrogen for one double bond was taken up. The reaction was then quenched and the liquid filtered off from the catalyst and the filtrate

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concentrated in vacuo. To destroy small amounts of the unreduced acid the solution was treated with permanganate until the red color of this salt remained longer than 15 min. A bisulfite solution was then added until complete decolouration and the cis-hexahydro-phthalic acid crashes out upon addition of some dilute sulfuric acid.

After one recrystallization from hot water, the compound gave a m.p. of 191 °C, which matched that specified by Baeyer.

\[
\text{4.967 mg Compound: 10.170 mg CO}_2, 3.13 \text{ mg H}_2\text{O.}
\]

\[
\begin{align*}
\text{C}_8\text{H}_{12}\text{O}_4 \quad \text{Calculated:} & \quad \text{C 55.8} \quad \text{H 7.0} \\
\text{Found:} & \quad \text{C 55.8} \quad \text{H 7.1}
\end{align*}
\]

This acid compound behaves towards bromine and sodium permanganate in the manner specified by Baeyer. To ensure its structure it was by heated for several hours with concentrated hydrochloric acid in a sealed tube at 180 °C, whereupon the trans-hexahydrophthalic acid rearranged.

\[
\text{5.086 mg Compound: 10.400 mg CO}_2, 3.22 \text{ mg H}_2\text{O.}
\]

\[
\begin{align*}
\text{C}_8\text{H}_{12}\text{O}_4 \quad \text{Calculated:} & \quad \text{C 55.8} \quad \text{H 7.0} \\
\text{Found:} & \quad \text{C 55.8} \quad \text{H 7.1}
\end{align*}
\]

The compound melts at 215–221 °C (Baeyer quoted 215–222 °C) and has the same solubility, crystal form and chemical behavior as the first acid characterized by Baeyer. It gives the corresponding anhydride upon heating with acetyl chloride with a m.p. of 142 °C (Baeyer quoted 140 °C).

\[
\text{4.958 mg Compound: 11.310 mg CO}_2, 2.83 \text{ mg H}_2\text{O.}
\]

\[
\begin{align*}
\text{C}_8\text{H}_{10}\text{O}_3 \quad \text{Calculated:} & \quad \text{C 62.3} \quad \text{H 6.5} \\
\text{Found:} & \quad \text{C 62.2} \quad \text{H 6.4}
\end{align*}
\]

The anhydride was converted by the procedure of A. Werner and Conrad E. to give the methyl ester acid with m.p. 94 °C (Werner quoted 96 °C) and the monamid with m.p. 194–195 °C (Werner quoted 196 °C).

\[
\text{Addition of Δ}^{1,3}\text{-dihydrobenzene to maleic acid anhydride (XIX).}
\]

\[
\text{IUPAC: 4-Oxatricyclo[5.2.2.0}_{2,6}\text{]undec-8-ene-3,5-dione}
\]

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A solution of 1 g of $\Delta^{1,3}$-Dihydrobenzene in 3 mL of benzene was prepared and 1.2 g of maleic anhydride was added. The reaction started after a few minutes and significant warming was observed. After a few hours the addition product precipitated out as a glittering, pure white crystalline mass. From the benzene mother liquor a second amount of addition product was obtained when the solvent was allowed to evaporate. The yield was quantitative. For analysis the crude product was purified by twice recrystallizing from middle-boiling ligroin.

**4.768 mg Compound: 11.780 mg CO$_2$, 2.42 mg H$_2$O.**

\[
\begin{array}{ccc}
C_{10}H_{10}O_3 & \text{Calculated:} & C \ 67.4 \quad H \ 5.6 \\
\text{Found:} & C \ 67.4 \quad H \ 5.7 
\end{array}
\]

The m.p. of the anhydride is 147 °C. What is striking is its resistance to boiling water. Even after several minutes of cooking it is recovered unaltered.

\(\alpha\)-Phellandrene and maleic acid anhydride (XX).

IUPAC: 10-(propan-2-yl)-4-oxatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-dione

7 g of maleic anhydride were shaken with 10 mL of benzene and 10 g of \(\alpha\)-phellandrene in a tightly sealed flask. The liquid immediately turned a yellow colour and heated up after a short time to ~ 40–50 °C; except for a small residue of the maleic anhydride everything went into solution. After a few hours, the mixture was filtered and the filtrate steam distilled \textit{in vacuo} over paraffin. The reaction product remained behind as a colorless crystalline mass and was best cleaned by recrystallization from boiling methanol. For analysis the compound thus obtained was dried \textit{in vacuo} at room temperature.

**4.949 mg Compound: 13.025 mg CO$_2$, 3.54 mg H$_2$O. — 4.701 mg Compound: 12.380 mg CO$_2$, 3.31 mg H$_2$O.**

\[
\begin{array}{ccc}
C_{14}H_{18}O_3 & \text{Calculated:} & C \ 71.80 \quad H \ 7.69 \\
\text{Found:} & C \ 71.81, 71.85 \quad H \ 8.00, 7.88 
\end{array}
\]

The compound forms large, glassy shard-like crystals of unusual beauty and melts at 126–127 °C.
5 g of citraconic anhydride dissolved in 5 mL benzene was treated with 3 g of cyclopentadiene; heat was evolved within a very short time. After several hours the reaction gave a product that was a viscous, slightly colored oil, but which solidified after 2–3 days in a desiccator to a white, compact, crystalline mass. For analysis the product was recrystallized twice from a large amount of petroleum ether. It formed a white, grainy crystalline substance with a m.p. of 138 °C.

5.037 mg Compound: 12.500 mg CO₂, 2.74 mg H₂O. — 5.181 mg Compound: 12.860 mg CO₂, 2.75 mg H₂O.

\[ \text{C}_{10}\text{H}_{10}\text{O}_3 \]

**Calculated:** C 67.42 H 5.62

**Found:** C 67.72, 67.73 H 6.08, 5.94

A solution of potassium permanganate in acetone is discolored instantly by the compound.

**Endomethylene-2,5-\(\Delta^3\)-tetrahydrobenzene-1-carbocarboxy-1carboxyl (XVIII).**

\[ \text{HOOC} \]
\[ \text{HOOC} \]

**XXIII**

IUPAC: 2-(carboxymethyl)bicycle[2.2.1]hept-5-ene-2-carboxylic acid

A suspension of 4 g of itaconic anhydride in the same amount of benzene was treated with 4–5 mL of cyclopentadiene. Heat was observed is the bulk of the anhydride enters solution. Upon completion of the reaction, undissolved residues were removed by filtration. Evaporation of the solvent yielded the anhydride of the title acid as a compact, colorless crystalline mass, which for analysis was recrystallized twice from boiling petroleum ether.

4.520 mg Compound: 11.220 mg CO₂, 2.35 mg H₂O. — 4.891 mg Compound: 12.100 mg CO₂, 2.55 mg H₂O.

\[ \text{C}_{10}\text{H}_{10}\text{O}_3 \]

**Calculated:** C 67.42 H 5.62

**Found:** C 67.71, 67.48 H 5.80, 5.83

The anhydride forms shimmering, snow-white needles; m.p. 53–54 °C. When placed in permanganate in acetone it is oxidized instantly.

For conversion into the free acid the anhydride boiled in water for as long as it took for all the oil to go into solution. The acid separated as crystals on cooling and was only moderately soluble in cold water. For analysis it was recrystallized again from hot water.

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5.180 mg Compound: 11.660 mg CO₂, 2.95 mg H₂O. — 4.825 mg Compound:
10.835 mg CO₂, 2.71 mg H₂O.

C₁₀H₁₂O₄  Calculated:  C 61.23  H 6.12
   Found:  C 61.40, 61.28  H 6.37, 6.26

The compound forms well-developed white crystals; m.p. 150–151 °C.

*Endomethylene-2,5-Δ⁴-tetrahydrobenzoic acid.*

7.5 g of pure acrylic acid were dissolved in about an equal volume of diethyl ether and to this
7–8 g of freshly distilled cyclopentadiene were added. The reaction mass warmed up to
~50 °C within a few minutes. The reaction was given several hours to proceed and upon
completion the solvent removed by evaporation to give an oily residue that was vacuum
fractionated. Upon heating, the flask contents temporarily turned green, and the first portions
to distill over were also coloured. The bulk of the distillate (12–13 g) came over at a pressure
of 22 mmHg at 132–134 °C.

The new acid forms a colorless oil of unpleasant odour, reminiscent in greater dilution of the
higher fatty acid odour. This oil solidifies on standing in a refrigerator to give a white,
crystalline mass that readily melts when warmed by the hands. A solution of sodium
permanganate instantly reduces the compound.

For analysis, the compound was again vacuum fractionated.

0.2516 g Compound: 0.6381 g CO₂, 0.1615 g H₂O.

C₈H₁₀O₂  Calculated:  C 69.57  H 7.25
   Found:  C 69.19  H 7.18

*Endomethylene-2,5-hexahydrobenzoic acid.*

A suspension of 7 g of endomethylene-2,5-Δ⁴-tetrahydrobenzoic acid in a little water was
mixed with a sodium carbonate in solution. After the evolution of carbon dioxide had ceased,
the 0.1 g of colloidal palladium was added to the mixture and it was shaken in a hydrogen
atmosphere at normal pressure; after 1 hour an amount of hydrogen had been taken up equal
to that calculated for one double bond. After completion of the reduction the majority of the
water was evaporated at 60–70 °C in a vacuum, the residue was then acidified with sulfuric
acid and the oily precipitate extracted into diethyl ether. The ether fraction was dried with
calcium chloride and the solvent then removed by evaporation to give the new acid as a
colorless oil, which distills at 13 mmHg at 125–127 °C and solidifies in the receiver as a pure
white, compact, crystalline mass. The new acid is virtually odorless in the solid state and is
sparingly soluble in cold water. From boiling acetonitrile the compound gives very large,
splendidly formed crystals; m.p. 62–63 °C.
4.880 mg Compound: 12.275 mg CO₂, 3.86 mg H₂O. — 5.018 mg Compound: 12.600 mg CO₂, 3.93 mg H₂O.

C₈H₁₂O₂ Calculated: C 68.57 H 8.57
Found: C 68.64, 68.52 H 8.85, 8.77

The acid is resistant to cold sodium permanganate solution.

\textit{Endomethylene-2,5-tetrahydrobenzaldehyde (XXII).}

IUPAC: Bicyclo[2.2.1]hept-5-ene-2-carbaldehyde

10 g of acrolein were dissolved in 15 mL of diethyl ether, 14 g of cyclopentadiene were then added to the mixture. The reaction starts after a few moments and gives vivid warming. After standing for several hours in a well-sealed vessel, the ether is distilled off and the residue, a pale colored oil, purified by fractionated under vacuum using a carbon dioxide stream. The bulk comes over at 70–72 °C under 20 mmHg pressure; 90–95% yield.

The new aldehyde forms a colorless, refractive extremely adherent, oil with a distinctive smell reminiscent of valeraldehyde.

It reduces ammoniacal silver solution instantly in the cold; the Schiff test gives only a slight reddening, while cold Fehling's solution is not attacked.

A conc. ether solution of the aldehyde will react with bisulfite in a few moments to give a snow-white bisulfite compound, from which the aldehyde can be regenerated by shaking in a warm soda solution. For analysis the compound was purified in this manner.

5.542 mg Compound: 15.880 mg CO₂, 4.16 mg H₂O.

C₈H₁₈O Calculated: C 78.69 H 8.20
Found: C 78.17 H 8.40

\textit{Semicarbazone.} A solution of 2 g of the aldehyde in alcohol were mixed with 2–2.5 g of semicarbazide hydrochloride and 1.1 g of sodium hydroxide in a little water; the semicarbazone crystallizes immediately as pure white crystals. After two recrystallizations from aqueous methanol it melts at 162 °C.

2.340 mg Compound: 0.464 mL N (18 °C, 757 mmHg).

C₈H₁₈ON₃ Calculated: N 23.5 Found: N 23.2

\textit{Condensation product with cyclohexanone.} A solution of the aldehyde (2.5 g, 20.5 mmol) and cyclohexanone (1 g, 10.2 mmol) were placed in 3–4 mL of alcohol and a few
drops of 30% sodium hydroxide solution were added. The reaction starts immediately and gives vigorous heat and requires several hours standing for completion. The reaction mass eventually solidifies to form a slurry of crystals, which recrystallize after pressing on clay in aqueous methanol; m.p. 105 °C. The product crystalizes very easily and has a pale yellow colour.

4.879 mg Compound: 15.370 mg CO₂, 3.84 mg H₂O. — 5.190 mg Compound: 16.370 mg CO₂, 4.04 mg H₂O.

C₂₂H₂₆O Calculated: C 86.27 H 8.50
Found: C 85.96, 86.06 H 8.81, 8.71

Endomethylene-2,5-hexahydrobenzaldehyde

14–15 g of endomethylene-2,5-Δ²-tetrahydrobenzaldehyde were dissolved in ~ 20 mL of alcohol and mixed with 0.2 g of colloidal palladium in a little water and shaken in a hydrogen atmosphere at ordinary pressure. Although the catalyst quickly flocculates, the reduction proceeds very smoothly and in ~ 2 hours the calculated amount of hydrogen for one double bond is taken up. After evaporation of the alcohol using vacuum and a carbon dioxide stream at about 30–35 °C, the hydrogenation product is taken up into diethyl ether, dried with calcium chloride, and the flocculated catalyst and CaCl₂ removed by filtration. The oily residue remaining after evaporation of the ether distills under vacuum with the carbon dioxide stream and comes over almost exclusively at 75–76 °C (25 mmHg). The distillate solidified when cooled by a cold water trap to give a mass of transparent, well-formed crystals that melt again even at low temperature. For analysis, the substance was once again fractionated under reduced pressure.

4.429 mg Compound: 15.410 mg CO₂, 4.68 mg H₂O.

C₆H₁₂O Calculated: C 77.42 H 9.68
Found: C 77.43 H 9.66

The aldehyde is characterized by an inherent and highly characteristic scent with a peculiar and refreshing nuance reminiscent of amy! alcohol; one that is also possessed by the camphor derivatives.

The new aldehyde forms a semicarbazone as easily as the tetrahydroaldehyde to give a m.p. of 141–142 °C; recrystallization from concentrated solutions readily gives an oily precipitate.

2.017 mg Compound: 0.398 mg N (19 °C, 757 mmHg).

C₆H₁₂OＮ₃ Calculated: N 23.2 Found: N 23.0

The easily prepared condensation product with cyclohexanone melts at 101–102 °C.

4.720 mg Compound: 14.735 mg CO₂, 4.20 mg H₂O. — 4.833 mg Compound: 15.070 mg CO₂, 4.29 mg H₂O.

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3–4 g of freshly distilled in a sealed tube butadiene are added to the same amount of acrolein and heated to about 100 °C in sealed tube for 1 hour*. After cooling the reaction product, a slightly coloured, thick amber oil was obtained and subjected to vacuum distillation using the carbon dioxide stream. After a small first fraction, which consisted largely of unaltered acrolein#, the main amount came over at 13 mmHg at 51–52 °C as a colorless, refractive oil. The remaining residue in the distillation flask formed a glassy foamy mass that apparently represented the polymers of the aldehyde. For analysis, the aldehyde was vacuum distilled once more.

5.268 mg Compound: 14.670 mg CO₂, 4.32 mg H₂O. — 4.838 mg Compound: 13.430 mg CO₂, 3.98 mg H₂O.

The aldehyde forms a colorless oil from a very characteristic scent that is reminiscent of isovaleraldehyde and benzaldehyde. Although it polymerizes rather readily when used, the compound can be stored for a long time without degrading.

*Semcarbazone. If an alcoholic solution of the aldehyde is treated with an aqueous solution of semicarbazide hydrochloride, the semicarbazone separates out immediately upon heating as a pure white crystalline mass. When recrystallized several times from highly diluted methanol it gives a m.p. of 153–154 °C.

2.252 mg Compound: 0.483 mL N (19 °C, 757 mmHg).

Then there can be no doubt that the aldehyde is identical to that described by W. Sobecki, prepared by a Grignard reaction of Δ³-bromocyclohexene and ortho-formic acid ester.

For conversion into the hexahydrobenzaldehyde, the semicarbazone of Δ³-Tetrahydrobenzaldehyde was catalytically reduced in a known manner. The alcoholic solution of the semicarbazone readily absorbs the calculated amount of hydrogen for one double bond to form the hexahydrobenzaldehyde semicarbazone; our observed melting point

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was 174–175 °C. Others in the literature have quoted: 167–168 °C (Wallach and Isaac); 173–174 °C (Zelinski and Gutt); 176 °C (Bouvault).

0.1194 g Compound: 26.30 mL N (23 °C, 748 mmHg).

\[
\begin{align*}
\text{C}_8\text{H}_{15}\text{ON}_3 & \quad \text{Calculated:} & \quad \text{N} & \quad 24.9 \quad \text{Found:} & \quad \text{N} & \quad 25.0
\end{align*}
\]

The hexahydrobenzaldehyde obtained from treating the semicarbazone with oxalic acid gave a m.p. of 158 °C (Gelding 161–163 °C, Zelinski 157–158 °C, Bouvalt 159 °C).

Concluded 14-Jan-1928