contained 0.449 %, the middle-liquid 1.952 % and the right-side liquid
3.498 % of tart.ac. We found that then 4.426 gr. of water had diffused
← o* and 5.421 gr. of water → and that 1.759 gr. of tart.ac. had diffused
through the bladder and 1.624 gr. of tart.ac. through the cellophane.

The systems (22) and (25) have practically the same invariant liquids,
the membranes, however, have been changed; as is apparent from the
arrows and the sign of Δm, this has a great influence on the osmosis; this
was indeed to be expected as also appears from the introduction. In (22)
the water diffuses inwards through both membranes and the quantity of
the stationary liquid increases continuously; in (25) the water diffuses
outwards through both membranes and the quantity of the stationary liquid
decreases continuously.

(To be continued.)


Chemistry. — The Formation of Cyclic Compounds of Pyrocatechol with
Aldehydes and Ketones. By Prof. J. BÖESEKEN and G. SLOOFF.

(Communicated at the meeting of December 17, 1932).

In aliphatic chemistry we know many condensation products between
diols (1.2 as well as 1.3) and aldehydes and ketones, compounds which
may be represented thus:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{R}_1 \\
\text{R}_2 \\
\text{O}
\end{array}
\]

Likewise similar compounds have been separated (especially with
acetone) with the hydromates. Of the aromates only pyrocatechol and
derivatives deserve consideration as regards formation of such compounds.
So far only the condensation product with formaldehyde, pyrocatechine
methylene ether was known. This compound was first prepared by
MOUREU 1), not by condensation of pyrocatechol with formaldehyde itself,
but through treatment of the sodium salt of pyrocatechol with methylene
iodide. Later also the cheaper methylene chloride was used. The amount
yielded is not given, but it is very small. There exists a good deal of
literature on the derivatives, among which safrole, piperonal, myristicine,
and apiole. In the study of these derivatives the natural products or
products derived from them (piperonal) are always taken as starting point.

Efforts to condense pyrocatechol with aldehydes or ketones have certainly
not been wanting, the more so as acetone is largely used for the deter-

mination of the constitution of diols and sugars\(^1\). Seeing the easy complex-formation of pyrocatechol with boric acid, which in general is accompanied by ready formation of acetone compounds\(^2\), it was to be expected that such a compound could also easily be made of pyrocatechol. Yet up to now this had never succeeded.

MEULENHOFF wrote about this\(^3\): "Of pyrocatechol itself so far no acetone compound has been separated, perhaps the catalyzer required for this, has not yet been found. Nevertheless it will probably be possible to prepare such compounds, although it be by another indirect way, the more so as some natural products possess a similar ring-system."

As catalyzers used were mentioned HCl, H\(_2\)SO\(_4\), and ZnCl\(_2\).

We could not imagine that the formation of an acetone compound of pyrocatechol would be impossible by the direct way.

A repeated experiment with H\(_2\)SO\(_4\) failed. On the other hand we succeeded with P\(_2\)O\(_5\). This mighty dehydrator was already used in 1906 by ALBARDA VAN EKENSTEIN and BLANKSMA\(^4\) in the condensation of mannitol with benzaldehyde.

Our first reactions were executed at a temperature of \(-10^\circ\) C. The yield of the condensation product was small\(^5\). A considerable improvement in the method was reached by working at higher temperature. Now we can prepare large quantities of acetone compound in a very simple way. The reaction was applied not only to acetone, but also to a series of other ketones. The yield obtained may be called good. The acetone compound is obtained in a yield of 65\%; di-n-propylketone, 67\%; methylnonylketone 72\%; cyclohexanone 80\%. All this calculated to the quantity of pyrocatechol which we started.

Aldehydes can also be condensed. So far we have prepared the acetaldehyde and the oenanthaldehyde compound, with yields resp. of 47\% and 45\%.

The usual way of preparation is as follows:

Pyrocatechol is dissolved in 2 or 3 times the required quantity of aldehyde or ketone. Then the temperature is raised so much that after addition of P\(_2\)O\(_5\) reaction just takes place, which appears from the P\(_2\)O\(_5\) becoming brown and sticky. In small portions a quantity of P\(_2\)O\(_5\) is added equal to twice that of the pyrocatechol used.

The acetaldehyde compound forms an exception. Here paraldehyde is

\(^1\) E. FISCHER. Ber. 28, 1167, 2496.
\(^2\) SCHULZ and TOLLENS. Ber. 27, 1892.
\(^4\) VAN LOON (loc. cit.) Diss. Delft 1919.
\(^5\) BOESEKEN. Rec. 41, 722.
\(^6\) HERMANS. Rec. 42, 1104.
\(^7\) MEULENHOFF. Diss. Delft, 1924.
\(^8\) ALBARDA VAN EKENSTEIN and BLANKSMA. Rec. 25. 153, 162.
\(^9\) BOESEKEN and SLOOP. These Proc. 35. 170 (1932).
started from, and all the $P_2O_5$ is added at once, after having the mixture of pyrocatechol and paraldehyde cooled to $-5^\circ$ C. By cooling now and then we ensure that the reaction takes slowly place.

The treatment of the reaction mixture is the same for all. The almost colourless liquid is poured off from the strongly brown-coloured $P_2O_5 + H_3PO_3$ mixture into diluted alkali, after which it is taken up by ether.

After the ether has been evaporated, it is fractionated under reduced pressure, in which first the excess of aldehyde or ketone goes over, then the cyclic aldehyde or ketone compound, which is immediately obtained very pure.

Here follow the boiling-points of the condensation products of pyrocatechol with the following aldehydes and ketones, all of them determined at a pressure of 20 mm. Hg.

Boiling points (Pr. = 20 mm.) of pyrocatechol with:

- acetaldehyde : 118°
- oenanthaldehyde : 155°
- acetone : 78°
- methyl ethyl ketone : 94°
- methyl-n-propyl ketone : 94°
- methyl iso propyl ketone : 102°
- methyl iso butyl ketone : 115°
- methyl nonyl ketone : 188°
- cyclo pentanone : 124°
- cyclo hexanone : 140°
- acetyl acetic ester : 155°
- methyl iso butyl ketone : 115°
- methyl nonyl ketone : 188°
- methyl iso propyl ketone : 102°
- methyl ethyl ketone : 94°
- acetone : 78°
- oenanthaldehyde : 155°
- methyl nonyl ketone : 188°

The lowest terms can be easily distilled with water-vapour. They are all liquids except the compounds with cyclohexanone and acetaldehyde, which have a melting-point of resp. $45^\circ$ and $32^\circ$. They all possess a peculiar aromatic odour. They are perfectly stable towards water. On boiling with 2 n HCl for about three minutes the acetaldehyde-compound shows a distinct colouring with FeCl₃, the acetone compound shows a faint colouring, whereas that of oenanthaldehyde and methyl nonyl ketone does not show any colouring at all.

Some derivatives of pyrocatechol can also be condensed with acetone. 3 nitro-pyrocatechol gives an acetone compound m.pt. $83^\circ$ 4 nitro-pyrocatechol a compound m.pt. $93^\circ$ 4 chlorine-pyrocatechol gives a liquid boiling pt. 750 mm $224^\circ$ 4.5 di-chlorine-pyrocatechol gives a compound m.pt. $88^\circ$.

The investigation will be extended to other substitution products of pyrocatechol.

The Acetone Compound of Pyrocatechol.

This compound is a colourless liquid with a peculiar smell. Melting-point $3^\circ$ C.

Boiling point 765 mm. 184°.

Specific Weight at $21^\circ$ 1.063.
Index of Refraction at 21.5° 1.5060.

Analysis gave the following results:
151.8 mg of substance gave 91.7 mg H₂O or 6.62 % H₂ (theoretically 6.66) and 400.1 mg CO₂ or 71.85 % C. (theoretically 72.00).

On nitration with nitric acid (sp. gr. 1.2), a yellow compound was obtained, which crystallizes out of alcohol in beautiful needles. Melt. pt. 93°.

This compound is identical with that obtained by acetonisation of 4 nitro­pyrocatechol. The yield of nitro compound is excellent. From 150 g. acetone compound, 180 g. nitro compound was obtained, i.e. 92 %. The reduction of the nitro-compound to the corresponding amine presented some difficulties. With tin and hydrochloric acid in aqueous solution splitting off of acetone was always observed, and only traces of the required amine were found. There are, however, formed large quantities of 4 amino pyrocatechol. Nor did some other reduction methods in aqueous solution lead to the desired result.

On the other hand it was obtained in ethereal solution with tin and hydrochloric acid. Yield 65 %. B. pt. 11 mm. 134—136° Melt. pt. 35°.

Analysis.
From 120.8 mg of substance are formed 72.5 mg H₂O or 6.50 % H₂ (calculated 6.67 %) and 288.4 mg CO₂ or 65.2 % C. (calculated 65.4 %).

The amine can be diaisotized in the usual way, and could be converted to some other derivatives.

On action of chlorine and bromine water on the acetone compound solid compounds were obtained with melt. pt. resp. 88° and 92°.

On closer examination the chloride appeared to be identical with the compound obtained by acetonisation of 4.5 dichlorpyrocatechol, and therefore the following structure should be assigned to it:

![Structure](attachment:image.png)

The Condensation Product of Acetyl Acetic Ester with Pyrocatechol.

It is a colourless compound with a disagreeable smell. B. pt. 20 mm. 155°.

Analysis.
137.2 mg of substance yield 77.0 mg H₂O or 6.23 % H₂ (calculated 6.30 %) and 324.5 mg CO₂ or 64.6 % C (calculated 64.86 %).

On nitration with HNO₃ (Spec. gr. 1.3) the mono-nitro compound is formed. Yield 90 % pure product. Light yellow compound, which becomes orange in the light. Melt. pt. 72°.

Analysis gave as result the expected compound C₁₂H₁₅O₆N.
150.2 mg of substance gave 65.6 mg H₂O or 4.85 % H₂ (calculated 4.87 %) and 296.4 mg CO₂ or 53.8 % C (calculated 53.9 %).

The acid belonging to this ester, is an asymmetric substance, and it must, therefore, be possible to split it up into optical isomers. Accordingly
this peculiar case of optical activity must arise on the introduction of a
substituent into the product of saponification of the ester obtained by
condensation of acetyl acetic ester with pyrocatechol. This case, which is
of course a special case of a series of similar compounds which may be
represented as follows:

\[
\begin{align*}
  & \text{X} \quad \text{O} \quad \text{C} \quad \text{R}_1 \\
  & \quad \text{O} \quad \text{C} \quad \text{R}_2
\end{align*}
\]

seemed to us a good object to execute the splitting.

We vainly tried to obtain the nitro acid by saponification of the above
mentioned nitro ester (Melt. pt. 72). On treatment with alcoholic potassium
(already in the cold) a potassium salt was deposited, to which on analysis
the formula \( \text{C}_{12}\text{H}_{14}\text{O}_7\text{N} \) appeared to be applicable.

On acidification we could obtain two different acids with melting-points
125° and 137° according to circumstances. On titration with barite we found
an equivalent weight of 267. Analysis gave a formula \( \text{C}_{12}\text{H}_{13}\text{O}_6\text{N} \).

The nitro acid which we sought, has a molecular weight of 240 and the
formula \( \text{C}_{10}\text{H}_9\text{O}_6\text{N} \). The ester from which we started, has a mol. weight
of 267 and the formula \( \text{C}_{12}\text{H}_{13}\text{O}_6\text{N} \).

It is clear that no saponification has taken place, but only a transposition,
in which a compound has been formed with acid properties.

Very probably ring-opening takes place. At present we are occupied with
trying to clear up this question 1).

When by this way the required acid could not be obtained, we followed
another method.

By saponification of the original ester the acid, a compound Melt. pt. 61°,
was obtained, and this was nitrated to the nitro acid sought. Compound
coloured light yellow Melt. pt. 125°.

201.5 mg. of substance consumed 10.88 cc. barite 0.0957 n. From this
is calculated a mol. weight of 194.2, must be 194.1 theoretically.

Analysis.

150.9 mg. of substance gave:
50.8 mg. \( \text{H}_2\text{O} \) or 3.74 % \( \text{H}_2 \) (calculated 3.79).
276.0 mg. \( \text{CO}_2 \) or 49.9 % \( \text{C} \) (calculated 50.2).

The position of the nitro group was found by heating the compound, in
which, with generation of \( \text{CO}_2 \), a yellow substance distilled, which solidi-
fied on cooling, and appeared to be the 4 nitro acetone compound (Melt. pt.
93°). \( \text{C}_9\text{H}_9\text{O}_4\text{N} \).

From the acid salts were prepared with some alkaloids. It then appeared

1) Herein we succeeded (see next communication).
that cinchonine was the most suitable substance for the splitting. With this in aqueous solution a well-crystallized compound is formed. The dextro-rotatory isomer is the least soluble, and could easily be isolated. From the first fraction of the salt the acid was again liberated by treatment with 2 n HCl. The rotation of this, measured in alcohol \( (\alpha_D) = +35^\circ \).

After a repeated treatment with alcohol, an acid was obtained, of which, after twice repeated recrystallization from chloroform, the rotation did not change any more. The rotation is then \( +41^\circ \) at 16\(^\circ\).

We have not yet obtained the laevo-rotatory component pure. The subsequent fractions of cinchonine salt give varying rotations, and still contain fairly much \( d \)-component.

The greatest laevo-rotation that we measured, was \(-37^\circ\).

_**Delft. November 1932.**_

Laboratory of organic Chemistry of the Technical Highschool.

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**Chemistry.** — _Die unbekannt gebliebenen Andreeaschen Präzisionsverfahren zur Dichtebestimmung fester Stoffe._ Von _ERNST COHEN und W. A. T. COHEn—DE MEESTER._

(Communicated at the meeting of December 17, 1932).


In Folgenden wird nur von solchen die Rede sein.

Die Veranlassung zur Veröffentlichung nachstehender Seiten ist die Tatsache, dass auch die neueste Literatur \(^3\) noch stets Mitteilungen bringt, deren Verfasser sich um das Auffinden eines Verfahrens bemühen, welches

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\(^1\) Z. physik. Chem. 3, 289 (1889); 4, 189 (1889); 11, 328 (1893).
