

Citation:

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Chemistry. — “*On the Condensation of Formaldehyde with some Unsaturated Compounds.*” By H. J. PRINS. (Communicated by Prof. J. BÖESEKEN).

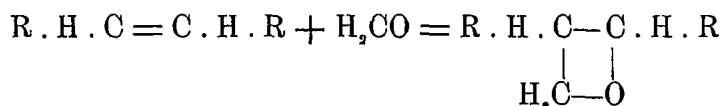
(Communicated in the meeting of May 3, 1919).

Some time ago ¹⁾ the author discussed the mutual condensation of unsaturated compounds, examining the condensation of formaldehyde with styrol, anethol, isosafrol, pinene, d. limonene, camphene and cedrene. The condensation was effected either by warming the components in acetic acid solution, or by sulphuric acid in an aqueous or acetic acid solution. For the aqueous solutions we availed ourselves of the 40% solution as supplied by the trade, the acetic acid solution was obtained by warming trioxymethylene in acetic acid with or without the presence of sulphuric acid.

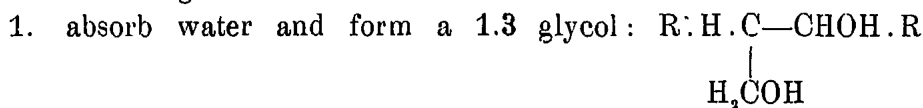
The aqueous and acetic acid solutions of sulphuric acid and formaldehyde behave differently as regards certain compounds, styrol, camphene and cedrene react but extremely slowly or not at all with the aqueous solution whereas anethol and isosafrol do react.

Contrary to isosafrol safrol does not affect an aqueous solution.

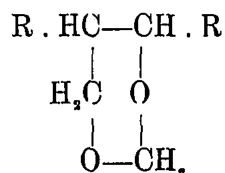
It may be assumed, that the reaction begins with an addition of the CO group to the C=C group, so that primarily a four-ring is formed.



The four-ring can now:

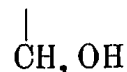


2. absorb formaldehyde and form a methylene ether:



¹⁾ Chem. Weekbl. 10, 1003 (1913).
ibid. 14, 932. (1917).

3. either directly by isomerisation, or indirectly via the glycol, pass into an unsaturated primary alcohol: $R \cdot C = CH \cdot R$



If acetic acid is also present, acetates may be formed either of the glycol, or of the unsaturated primary alcohol.

In an aqueous solution we find with anethol and isosafrol a pretty exclusive and almost quantitative formation of the methylene ether.

In an acetic solution in the presence of sulphuric acid both a diacetate and a methylene ether are formed, cedrene and camphene yield in these circumstances an acetate of an unsaturated, primary alcohol.

Camphene, d. limonene and pinene yield in an acetic solution at the boiling-point of acetic acid likewise an acetate of an unsaturated alcohol besides other compounds with a higher boiling-point.

The mutual reaction of formaldehyde, pinene and limonene causing the formation of an unsaturated primary alcohol has already been observed by KRIEWITZ¹⁾, who brought about a reaction of the components by heating them in the presence of alcohol at a high temperature.

Prior to this, the formation of a primary, unsaturated alcohol has been ascertained by LADENBURG in the reaction between formaldehyde and a tetrahydropyridine-derivate.

Except with the terpenes the condensation affords good results, ranging from 70% to 90%, of those theoretically possible; with the terpenes various products come into existence probably because the resulting unsaturated alcohol once more absorbs formaldehyde. The terpenes, containing more than one C = C group, there is besides a prior possibility of absorbing more than one molecule of formaldehyde.

The author likewise observed the setting in of suchlike reactions with amylene, citronellol, methylheptenon, citronellal, undecylenic acid, aethyl-cinnamate.

Experimental part.

Styrol and formaldehyde.

To a mixture of 33 gr. trioxymethylene and 320 gr. glacial acetic acid 32 gr. strong sulphuric acid was added, the trioxymethylene being solved by means of heating, then it was cooled down to 40° and while the mixture was shaken and occasionally refrigerated 104 gr. styrol was added in small quantities. If the temperature is allowed to rise beyond 50°, polymerization of the styrol sets in. The

¹⁾ Ber. d. deutsch. chem. Ges. 31, 57. (1899).

ibid,

32, 288, 2699 (1898).

mixture is allowed to remain overnight, then it is poured into water, taken up in ether and washed with a soda-solution. After drying and evaporating the ether, the diacetate amount can be determined by saponification. This proved to be 40 %. Then the oil is saponified with rather more than the theoretical quantity of alcoholic potassium and distilled in vacuum. By fractionation we can separate into:

Methylene-ether of 2.phenylpropylglycol. 1.3.

Colourless oil, boiling-point 128° — 130° , pressure 13 mm. $D_{40}^{180} = 1,1111$. $N_d^{180} = 1,53063$.

Mol. refr. 45.64 (formula of LORENZ—LORENTZ). Calculated 45.87 (atom refr. according to EISENLOHR ¹).

The molecular weight determination in benzene gave: 162 and 156. Calculated for $C_{10}H_{12}O_2$: 164.

Analysis: % C determ. 71.6 and 71.1 Calc. for $C_{10}H_{12}O_2$, 73.2.
% H determ. 8.3 and 7.9 Calc. 7.3.

2. Phenylpropylglycol. 1.3.

Colourless, viscous liquid, boiling-point 176° pressure, 13 mm. $D_{40}^{190} = 1.1161$. $N_d^{190} = 1.54267$. Mol. refr. 42.92. Calc. 43.21.

It yields quantitatively a diacetate boiling-point 162° — 164° pressure 13 mm. (chemically bound acetic acid determined by saponification with alcoholic potassium). Molec. weight of the glycol. in benzene 257 and 189. Calcul. 152. Hence it is very strongly associated in this solvent; in a weak solution a normal molecular weight is obtained ²)

Analysis: found % C 70,6 and 70,9, Calc. C, H, O, 71,0.
% H 9,2 and 8,9, Calc. 7,9.

Both methylene ether and glycol are saturated as regards a solution of bromine in CCl_4 , but while the methylene ether does not react with a solution of ethylmagnesiumbromide in ether at a normal temperature, the glycol immediately reacts. If toluol is added, raising the temperature to 100° , the methylene ether reacts exceedingly violently with the GRIGNARD solution. The fact that the glycol yields a diacetate when boiled with acetic acidanhydride and sodium-acetate is a proof of its two primary alcoholgroups, the isomeric-glycol, which might arise from the reaction between formaldehyde and the $C=C$ -group of the styrol, would be a secondary-primary glycol with the phenylgroup attached to the secondary carbon atom and in the above-mentioned circumstances it would certainly lose water

¹) Zeitschr. f. phys. Chem. 75, 585. (1910).

²) Chem. Weekblad 16, 929. (1919).

and yield the acetate of cinnamic alcohol. The latter could not be found.

Anethol and formaldehyde.

One grammol. anethol is stirred with a solution of two grammol. formaldehyde in 30% sulphuric acid for three days, the product separated in the usual way yields, when distilled in vacuum:

Methylene ether of p. methoxyphenylbutylglycol.

A colourless, viscous liquid, boiling-point 168° — 170° pressure 13 mm. $D_{40}^{160} = 1.1197$, $N_d^{160} = 1.53438$. Mol. refr. 57.78 Cal. 56,74.

It does not react with a GRIGNARD-solution at a normal temperature and does not decolorize a bromine-solution.

Various efforts made to saponify the methylene ether to the correspondent glycol failed, resinification always set in or the ether remained unaltered. By leaving the ether for a fortnight in contact with 85% formic acid, an oil was obtained, in which such an amount of formic acid was chemically bound as corresponded to 35% di-formate; saponification and distillation however, yielded an inconstantly boiling liquid.

Oxydation of the methylene ether.

In order to demonstrate, that with the anethol the formaldehyde had really reacted with the $C=C$ group from the side-chain, the methylene ether was oxydized with potassium-permanganate. An acid was obtained with a meltingpoint of 182° — 183° , and which revealed no depression when mixed with anisic acid.

Hence it appears, that in these circumstances formaldehyde does not react with the benzene nucleus.

Analysis of the methylene ether:

Found % C 70,1, 68,2 and 69,2. Calc. for $C_{11}H_{10}O$, 69,2.

% H 7,4, 7,8 Calc. 7,7.

Mol. weight in benzene: found 203 and 208. Calc. as $C_{12}H_{10}O_2$: 208.

Isosafrol and formaldehyde.

The condensation is effected in the same way as with the anethol.

It gives:

Methylene ether of 3,4 dioxymethylenephenylbutylglycol.

Colourless, viscous liquid, boiling-point 182° — 184° pressure 13 mm.

$D_{40}^{170} = 1,2272$. $N_d^{170} = 1,54078$.

Mol.refr. 56,84. Calc. 56,18.

Mol.weight in benzene: found 220 and 213. Calc. for $C_{12}H_{14}O_4$: 222.

Analysis:

Found % C 64,5 and 64,8. Calc. as $C_{12}H_{14}O_4$, 64,8.

% H 6,9 and 7,7. Calc. 6,3.

Camphene and formaldehyde.

A mixture of 30 gr. trioxymethylene, 130 gr. camphene and 136 gr. glacial acetic acid is boiled for three days, the oil separated by means of water, is dried, whereupon it is converted into an acetate by boiling it with an equal weight of acetic anhydride, which is called homo-camphenol acetate owing to its being derived from a homo-camphene.

Homo-camphenolacetate.

Colourless oil, boiling-point 124° — 128° pressure, 13 mm.
 $D_{40}^{190} = 1,0013$ $N_d^{190} = 1,48209$.

Mol.refr. 59.23. Calc. for a substance $C_{11}H_{18}O$, with one $C=C$ group: 59.02.

Homo-pinenol.

By boiling pinene with trioxymethylene and acetic acid in the way as indicated for camphene, an oil is obtained containing much chemically bound acetic acid, yielding after saponification and fractionation:

Colourless oil, boiling-point 113° — 116° in vacuo, pressure 13 mm.
 $D_{40}^{190} = 0,9720$. $N_d^{190} = 1,48616$.

Mol.refr. 49,05. Calc. for $C_{11}H_{18}O$ with one $C=C$ group 49,66, for $C_{11}H_{18}O$ with two $C=C$ groups: 51,39.

Mol. weight in benzene: found 188 and 190. Calc. 166.

Homo-limonenol.

Limonene is brought into reaction with formaldehyde in the manner as described for camphene, and the alcohol is separated as indicated for the pinene.

Colourless liquid boiling-point 122° — 126° in vacuo, pressure 13 mm. $D_{40}^{190} = 0,9757$, $N_d^{190} = 1,50261$.

Mol. refr. 50,26. Calc. for $C_{11}H_{18}O$ with two $C=C$ -groups 51,39.

Analysis.

Found % C 78,1 and 77,7. Calc. for $C_{11}H_{18}O$ % C 79,5.

% H 11,6 and 11,7. Calc. % H 10,9.

These results agree with those of KRIEWITZ, l.c.

Cedrene and formaldehyde.

A mixture of cedrene with the equivalent quantity of formaldehyde in a 15% solution of sulphuric acid in acetic acid, is stirred for three days. The reaction product is saponified and distilled in vacuum.

Besides other products with a considerably higher boiling-point there is obtained: Homo-cedrenol.

Colourless viscous liquid boiling-point 168° — 171° in vacuo, pressure 13 mm. $D_{40}^{19} = 1,0270$. $N_d^{19} = 1,51826$.

Mol. refr. 69,08. Calc. for $C_{16}H_{26}O$ with one $C=C$ -group 70,55.

As an alcohol it immediately reacts with GRIGNARD-solution and with acetylchloride, it discolorizes a bromine-solution.

Analysis.

Found % C 81,6 and 80,7. Calc. for $C_{16}H_{26}O$ % C 82,0.

% H 12,0 and 11,3. % H 11,1.

The principal aim of this investigation was: to demonstrate that formaldehyde reacts with a $C=C$ -group in the way as indicated in the author's general scheme for the reactions between unsaturated compounds.

Hilversum, April 1919.