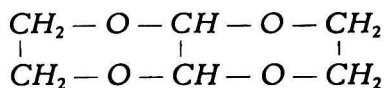


Chemistry. — *On the Two Isomeric Naphtho-Dioxanes 1.4.5.8*



an example of cis-trans isomerism in oxygenous six-rings of the decahydro-naphthalene type. By J. BÖESEKEN, F. TELLEGEN, and P. COHEN HENRIQUEZ.

(Communicated at the meeting of May 30, 1931.)

Introduction.

It may be considered as known (compare Proceedings 24, p. 202—204, 1921) that the absence of an increase of conductivity of boric acid by *cis*-cyclo-hexane diol 1.2, in contrast with the great influence exerted by the corresponding cyclo-pentane diols 1.2, was the first experimental confirmation of SACHSES¹⁾ conception of the tensionless rings with more than five atoms, also taking note of the suppletory interpretation of ASCHAN that they must be imagined as mobile²⁾, to avoid the consequence that when the atoms do not lie in the same plane, stereo-isomers are possible, which have never been separated yet.

The hydroxyl groups at vicinal C-atoms, of which it had been proved by another way, that they repel each other, can then lie apart as far as possible and in the *cis*-position, they even lie unfavourably for the ready formation with boric acid and acetone of five-membered ring systems. That these five-membered rings can be formed, must be accepted as an experimental proof of the mobility of the *six*-membered rings.

In the *trans*-cyclo-hexane diols 1.2 the position of the hydroxyl groups is still more unfavourable and it can easily be demonstrated by the atom models that with the movements of the molecule they will never reach such a position that a five-ring e.g. with acetone will easily be formed. In fact HERMANS³⁾ found no indication of the formation of a cyclic aceton compound.

Yet five-ring formation with groups in a 1.2 *trans*-position of a saturated six-ring must be possible, witness the separation by BAEYER⁴⁾ of the anhydride of *trans* cyclo-hexane-o-di-carbonic acid, though it is possible that the combination of the two rings is not tensionless in this case.

If two saturate *six*-ring systems are in question, the chance to ring closure in the *trans*position becomes considerably greater, and the separation of

1) SACHSE, Berichte 23, p. 1363; Zeitschr. physik. Chem. 10, 228 (1890).

2) O. ASCHAN, Alicyclische Verbindungen, p. 328—338.

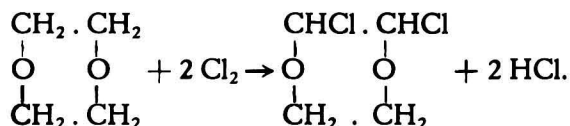
3) P. H. HERMANS, Zeitschr. anorg. Ch. 142, p. 90 (1924).

4) Annal. 166, 350 (1873), 258, 214 (1890).

the two decahydronaphthalenes by HÜCKEL and the study of their derivatives¹⁾ were a welcome supplement of our experiments and a corroboration of our views.

In the study of the chlorination of dioxane and of the reactionproducts of the dichlorodioxane obtained, we met with a case of isomerism, which is explained in the simplest way by the assumption of two stereo-isomers in the same way as the two deca-hydronaphthalenes of HÜCKEL.

The dioxane, the cyclic anhydride from two molecules of glycol, which is at present technically prepared on a large scale, can be very well chlorinated; two hydrogen atoms are then replaced by chlorine atoms:



That these chlorine atoms are bound to vicinal carbon atoms can be proved by decomposing this substance with water; we then find one molecule of glycol and one molecule of glyoxal



which could be proved by determining this last substance as *di*-(nitrophenyl) osazone.

These chlorine atoms are very mobile; with sodium alcoholate the vic. di ethyl ether of dioxane is formed quantitatively; this aether is a very stable compound.

When di chloro dioxane is heated with glycol in benzenic solution, hydrochloric acid is generated. When after the reaction the benzene is evaporated off, a crystalline mass remains, which, after systematic recrystallisation from alcohol, can be separated into two substances, melting resp. at 133°—136° and 109°—112°, neither of which are accordingly quite pure yet, but of which the analyses and the determination of the molecular weights leave no doubt but we have to do with two isomers. In view of the synthesis these can hardly be anything but stereo isomers, which may be represented by the symbols. (See Plate).

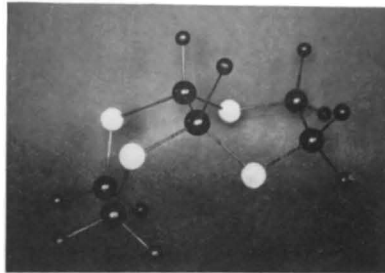
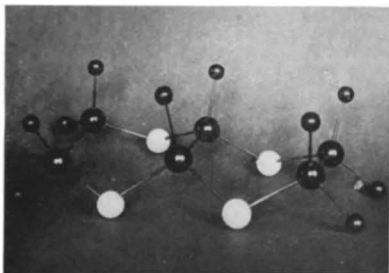
As the name: "di-dioxane" might give rise to confusion, we propose to designate the substances as *cis*- and *trans-naphtho-dioxane*, leaving it for the present an open question which is the *cis* and which the *trans*.

It is our intention to continue the study of these compounds and their derivatives in different directions. Just as the substitution of an oxygen atom for a C-atom does not greatly modify the rigidity of the *five*-ring²⁾, so the pliancy of the *six*-rings does not change by the introduction of oxygen atoms in the ring.

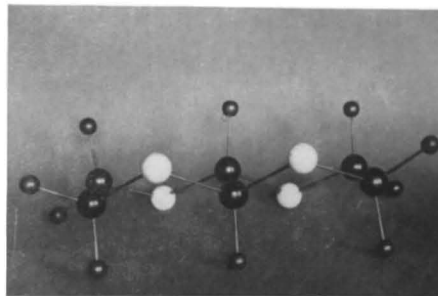
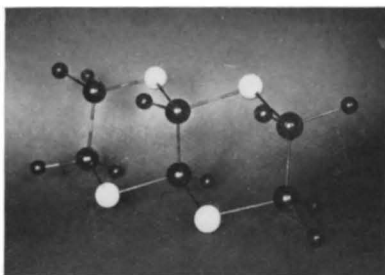
¹⁾ W. HÜCKEL, *Annal.* **441**, 1 (1925), **451**, 9 (1926). Cf. E. MOHR, *Journ. of pr. Chem.* **II**, **98**, p. 315 (1918), and *Berichte* **55**, p. 230 (1922).

²⁾ „De stereochemie der Wijnsteenzuren”. Proefschrift J. COOPS, p. 60 and *These Proc.* **28**, p. 374 (1925).

J. BÖESEKEN, F. TELLEGEN AND P. COHEN HENRIQUEZ:
ON THE TWO ISOMERIC NAPHTHO-DIOXANES 1.4.5.8.



Cis-naphtho-dioxane 1.4.5.8



Trans-naphtho-dioxane 1.4.5.8

Special and Experimental Part.

Dioxane has been known for a long time. LORENCO¹⁾ obtained it from glycol and ethylene bromide. WURTZ from liquid ethylene oxide²⁾ with bromine. We prepared it according to FAWORSKY³⁾ by slow distillation of glycol, to which 4% conc. H₂SO₄ had been added; we freed it from the by-products acetaldehyde and cyclic acetal of glycol with acetaldehyde by careful fractionation. The method of VAN ALPHEN⁴⁾ from glycol and ferri-sulphate gave us no better yield. By FAWORSKY'S method we obtained 30%, according to VAN ALPENS 15—20%.

200 cc of glycol mixed with 7 cc of conc. H₂SO₄ was heated to its boiling point, and then 300—400 cc of glycol from a funnel were added in drops. At $\pm 100^\circ$ a mixture distils over which is separated into two layers on addition of calcium chloride. The upper layer chiefly contains the dioxane: it is dried on CaCl₂, and then fractionated. The lowest-boiling fraction is chiefly the cyclic glycol-acetal, boiling point 84° — 85° ; the highest-boiling fraction b.p. 100° — 101° is the dioxane.

Of dioxane several addition compounds are known. WURTZ (loc. cit.) obtained dioxane dibromide C₄H₈O₂Br₂, melting point 65° — 66° , a light brown compound. Also with iodine, ICl and IBr addition compounds of the same type have recently been separated⁵⁾.

A corresponding *di*-chloride is not known. If chlorine is led into dioxane, it at first readily dissolves without coloration; only later a yellow coloration sets in. It is very probable that at first an addition product is formed. Very soon after, however, the formation of hydrochloric acid sets in, that is to say: substitution takes place, so that the separation of dichloride is probably only possible when chlorine and dioxane are added in an indifferent medium at low temperature.

We have executed the substitution reaction by leading chlorine at 90° into dioxane which was put in a spiral washing flask, 85 gr. could be chlorinated in this way in 16 hours⁶⁾. A colourless liquid was then formed, which was readily decomposed by water on account of the mobility of the chlorine atoms. After removal of the dissolved Cl₂ and HCl by heating, dry pyridine was added, to remove the last rests of HCl; it was diluted with dry ether; then C₅H₅NHCl was precipitated, and the liquid was distilled in vacuum.

First unchanged dioxane went over (12 gr.), and then 90 gr. of dichloro-dioxane b.pt. $82^\circ.4$ at 14 mm. Not a trace of monochloro-dioxane was found, not even when we had purposely taken an excess of dioxane.

1) Ann. de Ch. 3, 67, 284, 288 (1863).

2) Ann. de Ch. 3, 69, 323 (1863).

3) Zent. Blatt. 1907, I, p. 15.

4) Recueil 49, 1041 (1930).

5) RHEINBOLDT and BOY, Journ. f. pr. Chem. [2] 129, p. 273 (1931).

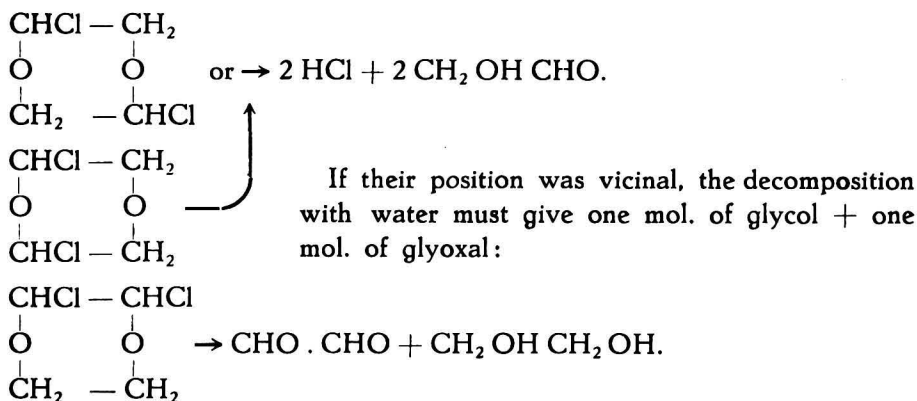
6) We feel it as a pleasant duty to express our indebtedness to Mr. P. MALTHA for his assistance in the systematic investigation of the best conditions for this reaction.

Analysis.

0.0944 gr. of substance gave 0.1705 gr. of AgCl found 44.7 } calc. for
 0.167 " " " " 0.3052 " " " " 45.2 } C₄H₆O₂Cl₂, 45.2%.

In order to find out to what C-atoms the chlorine atoms were bound, the compound was decomposed with water, which takes place quickly and quantitatively on gentle heating.

If the two chlorine atoms were situated at the places 2—5 or 2—6, nothing but glycolaldehyde could have been formed :



As the aqueous solution gave with p-nitro-phenyl-hydrazine *in the cold immediately* the di(nitrophenyl) osazone (m. p. 309°) in about the calculated quantity for one molecule :

0.2397 gr. of dichlorodioxane gave 0.4924 gr. of oxazone, calculated 0.500 gr.
 0.1833 " " " " 0.3739 " " " " 0.381 "

and the reactions with glycolaldehyde proved negative, we have to do with 2.3 dichlorodioxane. Presumably this is a mixture of the two stereo isomers, though nothing appeared of this in the distillation¹⁾.

If the dichlorodioxane is brought together with an anhydrous alcoholic solution of NaOC₂H₅ in the ratio of 1:2 mol., NaCl splits off with generation of heat; after centrifugation of the precipitate and evaporation of the alcohol, a colorless liquid, with a pleasant smell, readily soluble in alcohol and dioxane, but not easily soluble in water, distils over at 96°—97° and a pressure of 15 mm.

Analysis :

0.0895 gr. give 0.1774 gr. of CO₂ and 0.0743 gr. of H₂O } Found C=54.1 and
 0.1345 " " 0.2660 " " " " 0.1105 " " " " } 54.0%;
 } H = 9.2 and 9.1 %
 } Calculated C=54.5 "
 } H = 9.0 "

¹⁾ It is very probable that at the boiling point the two stereo isomers form an equilibrium mixture, also in gaseous condition, under the influence of the hydrochloric acid, which is always present.

This substance, very probably 2.3 dioxane *di* ethyl ether, is very stable, is e.g. not hydrolysed by boiling with diluted acids (no reduction).

Preparation of the Naphtho-dioxanes 1.4.5.8.

In dry benzene dichloro-dioxane is boiled with a slight excess of glycol for 16—20 hours at a reflux-refrigerator with CaCl₂-tube, till the formation of hydrochloric acid has ceased. Then it is cooled, poured off from the slight quantity of glycol which is insoluble in benzene, and the excess of benzene is evaporated at 30° in vacuum. There then remains a somewhat soft crystalline mass, which is recrystallised out of the sevenfold quantity of alcohol; the crystals now present a melting range of 85°—110°. After having been again dissolved in alcohol in the same way, they are crystallised out in fractions; after a twice repeated recrystallisation the *first* fraction has a melting-point of 133°—136°. Now follow a few intermediate fractions with larger melting ranges; after having been twice recrystallised the *last* fraction has a melting point of 109°—112°.

Analyses	Found	Calc. for C ₆ H ₁₀ O ₄
I. Mixture, melt. range 87°—120° 16.05 mgr. gave 28.91 mg. CO ₂ and 9.94 mg. H ₂ O	C = 49.1; H = 6.9	C = 49.3; H = 6.8
II. Highest-melting substance Mpt. = 133—136° 20.21 mg. gave 36.75 mg. CO ₂ and 12.38 mg. H ₂ O 17 " " 30.40 " " " 10.55 " "	C = 49.6; H = 6.8 C = 48.8; H = 6.3	" "
III. Lowest-melting substance Mpt. 109°—112° 14.43 mg. gave 26.06 mg. CO ₂ and 9.03 mg. H ₂ O	C = 49.3; H = 6.9	" "

Cryoscopic determination of the mol. weight according to Rast in camphor.

	Depression	Found	Calculated
Highest-melting substance, 8.2 mg. dissolved in 98.0 mg. campher.	22°.4 C.	149	146
Lowest-melting substance, 6.0 mg. dissolved in 99.6 mg. campher.	15°.2 C.	158	

It follows from this that we have to do with isomers, and on the strength of the way of formation, with stereo isomers of the decahydro-naphthalene type.

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the Technical University.*

Delft, May 1931.