

colourless rhodium- and platinum-complexes derived from these optically-active bases.

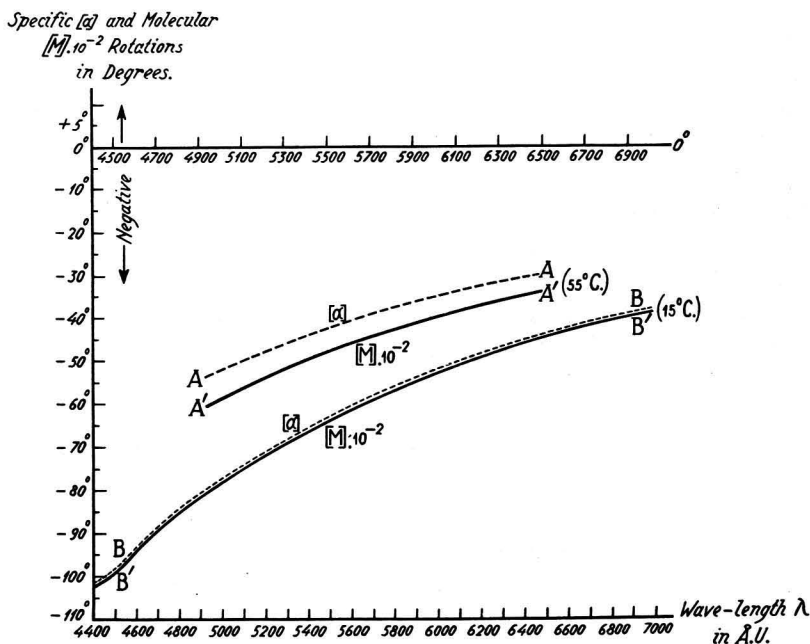


Fig. 10. The Rotatory Dispersion of the optically-active Cyclohexanediamines. (The curves B relate to the corresponding Cyclopentanediamines).

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Chemistry. — *Some properties of unsaturated sulphones.* By J. BÖESEKEN and E. DE ROY VAN ZUYDEWIJN.

(Communicated at the meeting of November 28, 1936).

In a previous communication¹⁾ one of us (B) pointed out that a saturated five-ring, exclusively consisting of carbon atoms, corresponds with regard to its properties with the analogous, non-cyclic saturated compound. This applied to the α -hydroxy-carbonic acids, where was stated by means of their behaviour towards boric acid that the ring closure did not alter the position of hydroxyl and carboxyl groups with respect to each other.

From measurements of the conductivity of mixtures of boric acid with cyclopentane-cis-hydroxy-carbonic acids²⁾ it might even be concluded that in this ring there must still be some flexibility, allowing the adjacent

¹⁾ Proc. Royal Acad. Amsterdam, 39, 28 (1936).

²⁾ J. BÖESEKEN, G. SLOOFF, J. M. HOEFFELMAN and H. E. HIRSCH, Recueil trav. chim. 52, 881 (1933).

hydroxyl and carboxyl groups to deviate. It may be remarked here that CHR. VAN LOON³⁾ already in 1919 by comparing the behaviour of cis-cyclopentane diols, cis-hydrindene diol and pyrocatechol towards boric acid observed that "by the benzene ring the hydroxyl groups are pressed into one plane, so that a ring of five carbon atoms possesses a smaller degree of rigidity than is usually supposed".

If in the five-ring a double bond is present or if it is fixed to a benzene ring (CHR. V. LOON) or two five-rings have three C-atoms in common²⁾, the situation is changed, the flexibility has decreased, the derivatives must differ from the corresponding non-cyclic compounds or from the simple saturated ring systems respectively. This became apparent in the first place from boric-acid measurements and as far as unsaturated cyclic hydrocarbons are concerned from measurements of the velocity of reaction with peracetic acid, from which might be concluded that in cyclopentene a ring tension was present⁴⁾.

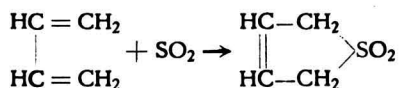
We now have asked what will be the result of the substitution of one of the C-atoms by another atom or another group of atoms.

It is a well-known fact that saturated five-rings with one atom of oxygen or of nitrogen display a great stability and the boric-acid measurements of the cis-diols derived from them show that conditions are found analogous to those of the corresponding cyclopentane diols.

We may point here to α -mannitan which causes a considerable increase of the conductivity of boric acid⁵⁾ and to N-ethyl antitartrimide, the influence of which is still somewhat larger⁵⁾.

Since we know now for certain that these increments are in direct connection with the position of the cis-placed groups in space, we may conclude that the substitution of one of the ring-forming atoms by another does not make an essential difference to the steric condition of the ring. The quantitative change points to a more rigid structure of these rings in comparison to the saturated ring which exclusively consists of C-atoms.

Sterically oxygen and nitrogen are situated close to carbon. Consequently it will be more interesting to examine substances in which one of the C-atoms has been substituted by a group, strongly deviating from the carbon and from the adjacent atoms in the natural system, both in mass and in nature. An opportunity to do this was offered by the discovery of a remarkable addition-reaction⁶⁾, that of SO₂ at the ends of a conjugated system:



³⁾ CHR. V. LOON, Thesis Delft 1919, p. 52.

⁴⁾ J. STUURMAN, Thesis Delft 1936. J. BÖESEKEN and J. STUURMAN, Proc. Royal Acad. Amsterdam, 39, 3 (1936).

⁵⁾ Proc. Royal Acad. Amsterdam, 28, 372 (1925). See also N. VERMAAS, Rec. trav. chim. 51, 82 (1932).

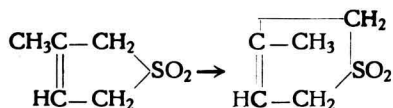
⁶⁾ EIGENBERGER, J. pract. Chem. [2] 127, 307 (1930); 129, 312; 131, 289 (1931).

This addition-reaction takes place fairly quantitatively at room-temperature and is an example of the binding of a single atom to two atoms which in normal condition lie rather far apart in space. Since these generally well crystallizing cyclic compounds at a rise of temperature decompose into the two components, they may serve both for the quantitative determination of substances with a conjugated system and for their purification.

Moreover, from the easy decomposition it appears that a tension is present in this molecule, since in the saturated, not ring-shaped sulphones the C—S bond is exceedingly firm.

EIGENBERGER proved the composition of these cyclic sulphones; he found besides that in the presence of KOH by ultraviolet light they were changed into isomers.

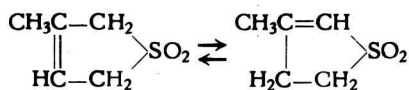
Owing to the fact that, on decomposition with metallic potassium, these isomers behaved in the same way as the original substances, he concluded that we have to deal here with a case of cis-trans isomerism:



On examination of the latter molecule in space, we see that very high tensions must be found in it, at any rate far higher than in the original molecule.

These isomers now happen to be much stabler than the original products, so that the configuration suggested by EIGENBERGER must be considered highly improbable.

A shifting of the double bond to the SO₂ group under the influence of the alkali seemed therefore much more likely.



Indeed, this structure has been proved by us by means of the ozonization-reaction, the isomerization thus being reduced to a conceivable shifting.

Considering that shifting of a double bond to an acidifying group under the influence of alkalis has been repeatedly stated, it was obvious that the alkali should be considered as the actual cause and *not* the light. The conversion indeed takes place also in the dark, only much more slowly: the ultraviolet light has exclusively an accelerating action.

At about the same time STRATING ⁷⁾ proved the structure of the isomeric cyclic sulphones, namely by application of the particular ozonization method found and described by us ⁸⁾.

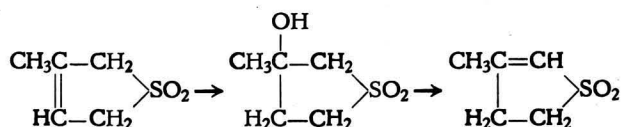
It was further found by STRATING and by us that, if the double bond of

⁷⁾ J. STRATING, Thesis Groningen 1934.

⁸⁾ Rec. trav. chim. **53**, 673 (1934).

the original sulphone no longer carried an H-atom, the conversion did not take place.

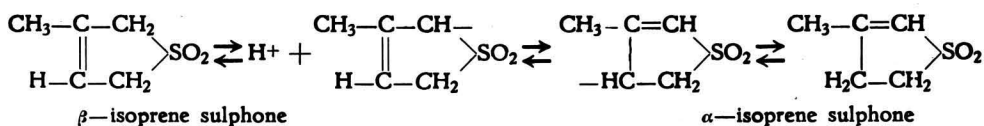
Since by the conversion always a hydrate was formed, BACKER and STRATING⁹⁾ thought that this should be regarded as an intermediate product:



in such a way that the OH group should be bound to the tertiary C-atom. On separation of H₂O, (possibly by the side of the original sulphone) the isomer should be formed, of which the position of the double bond, as stated above, had been established by their (and by our) researches.

If two alkyl groups were situated on either side of the double bond, the water molecule would be split off again in the same way.

We could prove that, under the conditions of the experiment, the hydrate remained unaltered, so that it may not be regarded as an intermediate product. The explanation should, therefore, rather be sought in the activation of an H-atom by the side of the SO₂ group¹⁰⁾, which then is split off as a proton, causing the formation of a negative ion. It has to be assumed here that the H-atom of the CH₂ group between the SO₂ and the C—CH₃ group is most easily activated and that subsequently the =CH group becomes the carrier of the electron; this takes up the proton again.



If there is no =CH group in the β-position, the proton returns to its old place.

Although objections may be raised to this theory, it is conceivable that it is a reversible process. We showed this, since the same final condition was obtained by starting both from the β- and from the α-isoprene sulphone. This was found by determination of the melting-point of the mixture which was ultimately obtained, after the melting-point curves of the two isomers had been determined.

At 30° this equilibrium lies at c. 91% of the α- and 9% of the β-sulphone. The equilibrium of the cyclic butadiene sulphones could not be determined in this way, since the formation of the hydrate (see above) made this impossible.

Yet, it could be stated qualitatively that we have to deal here also with

⁹⁾ Rec. trav. chim. 54, 618 (1935).

¹⁰⁾ C. K. INGOLD and C. W. SHOPPEE, J. Chem. Soc. 1929, 1199.

a reversible process, since the α -sulphone, derived from the β -sulphone, after complete purification, was again partly transformed into β -sulphone by means of alkali. After some time, on careful heating, butadiene and SO_2 were obtained, which is only possible if β -sulphone has been formed again.

We have further asked: is there any connection between this isomerization and the ring-structure? If this is not the case, non-cyclic β -unsaturated sulphones must also show this phenomenon. For this purpose we have synthetically constructed several of these compounds but, while hydration was stated, we observed nothing whatever of a shifting of the double bond.

This shows partly again that hydration is in no way connected with the shifting, partly that the unsaturated ring indeed exerts a pressure on the double bond in order to take a position which is more favourable to the stability.

That in these unsaturated cyclic sulphones a tension may be expected can be inferred from the steric conditions of such a ring-system, which correspond to those of the cyclopentenes; the unknown factor lies here in the SO_2 group.

We thought that, in connection with STUURMAN's research (l.c.) on the velocity of oxidation of the cyclenes with peracetic acid, here also by means of a similar study from the values B and E in ARRHENIUS' relation:

$$\log K = -\frac{E}{2.303 RT} + B$$

a tension might be derived. However, the velocity of oxidation was exceedingly small (influence of the SO_2 group), but what was worse, irregularities were found which made it impossible to obtain any results in this way. Moreover, the supply of good comparable material for investigation met with great experimental difficulties.

For this reason we followed a more qualitative method. If it can be demonstrated that the saturated cyclic sulphone is less flexible than cyclopentane, it follows that in the unsaturated cyclic sulphone a tension occurs which is at least equal to that in cyclopentene. We tried to attain this by determination of the increase of conductivity of boric acid under influence of the cis -2.3 dihydroxy cyclosulphones.

The diols were prepared by oxidation of the unsaturated cyclic β -sulphones with KMnO_4 or $\text{KClO}_3 + \text{OsO}_4$, in which case indeed glycols were formed which increased the conductivity.

If this oxidation was performed with peracetic acid, the isomers were formed which were indifferent to boric acid.

From this result it appears that in case of the first method of oxidation the hydroxyl groups are placed on the same side of the ring, whereas with peracetic acid they come to be situated on either side. Consequently the very peculiar SO_2 group does not alter the steric course of these oxidations, an observation which highly raises the diagnostic value of these methods of oxidation for steric purposes.

Another remark may follow here. In oxidations with peracetic acid the primary oxidation product nearly always appears to be the oxide¹¹⁾. This oxide is formed by saponification with KOH of the mono-acetate of the diol obtained with peracetic acid, but can *not* be saponified into the diol by means of acetic acid. Here the very stable oxide is certainly not the intermediate product and the diol acetate must be the primary product¹²⁾.

Comparing the obtained increments of the conductivity with those of other ring systems (see table):

Increase of the conductivity of 0.5 m H₃BO₃ by some five-ring diols at 25°
(KOHLRAUSCH—HOLBORN $\times 10^{-6}$).

Diol	C	Δ	Observations
cis-butadiene sulphone 2.3 diol	0.5 m	+ 494	The isomers with transplacated hydroxyl groups do not exert a positive influence on the conductivity of boric acid.
cis-isoprene „ 2.3 diol	0.5 „	+1096	
cis-dimethyl butadiene sulphone 2.3 diol	0.5 „	+1458	
ethylimide of anti-tartaric acid	0.2 „	+ 702	
α -mannitan	0.2 „	+ 772	
cis-cyclopentane diol 1.2	0.5 „	+ 149	
methyl 1 cis-cyclopentane diol 1.2	0.5 „	+ 114	
hydrindene diol 1.2	1/7 „	+ 63	

We see, taking into account the chosen concentrations, that the cyclic sulphonedioles correspond more with the heterocyclic than with the isocyclic five-ring systems. With regard to what has been said in the introduction, it follows that the hydroxyl groups are more favourably situated to form complex boric-acid compounds.

This may have either a purely steric cause, a more rigid state of the five-ring, impeding the mobility of the hydroxyl groups, or an energetic one, brought about by the nature of the hetero-atoms in the ring.

Considering that the oxygen atom in the α -mannitan, the imid group in the tartrimid and the sulphone group in the cyclic sulphones, groups which differ so much in nature, exert an analogous influence on the formed complexes, it is obvious, of course also taking into consideration all other researches in this field, that mainly steric factors must be assumed. If we accept this supposition, the saturated sulphones will have a somewhat more rigid structure than the simple cyclopentanes, and the unsaturated cyclic sulphones will possess a considerable tension. Determination of the heat of combustion of these compounds and of their saturated hydration products would here undoubtedly give the desired explanation.

¹¹⁾ J. BÖESEKEN and G. C. C. SCHNEIDER, Journ. f. pr. Ch. N. F. **131**, 285 (1931).

¹²⁾ It is possible that first a labile oxide is formed.