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Cyclische sulfonen en selenonen, derivaten van butadieenen

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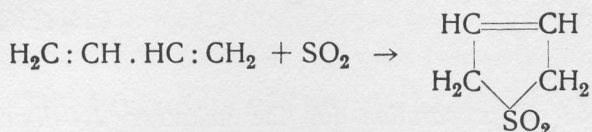
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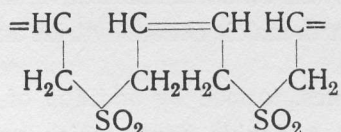
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VII. SUMMARY OF THE RESULTS.

For the *preparation of cyclic sulfones* a general method has been found in the heating of butadienes with a solution of sulphur dioxide in ether. Addition takes place according to the equation:



The formation of *polymerisation products* with the lower terms can be avoided by bringing the oven beforehand to the temperature required. This measure is not sufficient to form butadiene sulphone; addition of a so-called anti-catalyser is necessary, the most suitable being pyrogallol. According to Staudinger, the formation of polymerisation products takes place as follows:



With the higher homologues, from the 1,2,3,4-tetramethyl butadiene-1,3, the formation of this type of by-product has not been observed.

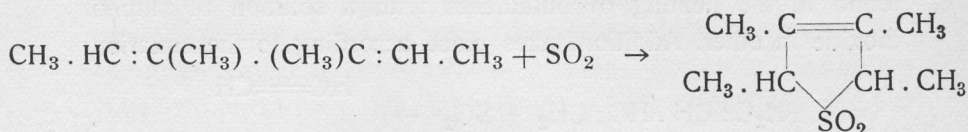
The sulphones with the simple formula are well-crystallized and fairly stable compounds. When heated above their melting points, they are *decomposed* into their component parts.

By means of *potassium permanganate* the sulphones are further oxidized via the dihydroxy compounds.

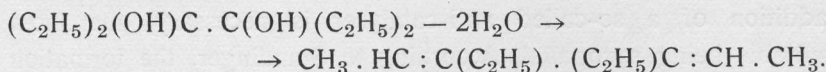
They are very stable against *absolute nitric acid*, in which most dissolve unchanged. Thus, for a sulphur determination according to Carius, special measures have to be taken. Heating for 36 hours at 370° is necessary to complete the oxidation.

Whitby and Macallum's supposition, that the introduction of two methyl groups on the places 1 and 4 of butadiene would prevent the formation of a sulphur dioxide addition-product, has proved to be *wrong*.

1,2,3,4-Tetramethyl and 1,4-dimethyl-2,3-diethyl butadiene-1,3 with sulphur dioxide yield the corresponding cyclic sulphones.



A *method of preparation* for the unknown 1,4-dimethyl-2,3-diethyl butadiene-1,3 has been found in the removal of water from diethylketone pinacone. This is a general method to obtain symmetrically alkylated butadienes:



In order to identify this butadiene derivative, the addition products have been prepared with maleic acid anhydride and α -naphthoquinone.

The cyclic sulphones, formed by addition of sulphur dioxide to butadienes, all have a *double bond*, which can be demonstrated with potassium permanganate.

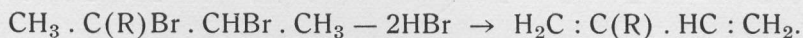
Addition of bromine does not take place in all cases; it depends on the substituents attached to the doubly-bound carbon atoms. Failing of addition, which is to be ascribed to steric obstruction, is caused amongst others, by two tertiary butyl or phenyl groups, whilst a chlorine atom and a methyl group together also prevent the addition of bromine or chlorine.

Attention should be drawn to the fact, that one tertiary butyl group can also prevent the addition of bromine, whereas one phenyl group has no perceptible negative influence on the addition. This is shown clearly in the reaction of bromine with the sulphones of 2-tertiary butyl butadiene-1,3 and 2-phenyl butadiene-1,3. To the

former sulphone no bromine is added, to the latter the addition succeeds easily.

For the investigation of the *isomerism*, which Eigenberger observed by exposing the isoprene sulphone to ultra violet rays, it was necessary to make some butadienes analogous to isoprene.

Two such compounds were prepared. Their formation is based upon a catalytic removal of hydrogen bromide from the corresponding dibromobutane or bromobutene. In this way *2-phenyl butadiene-1,3* and *2-tertiary butyl butadiene-1,3* were prepared.

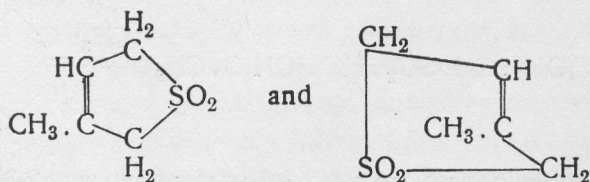


In order to identify these hydrocarbons, the addition compounds with maleic acid anhydride and α -naphthoquinone were prepared.

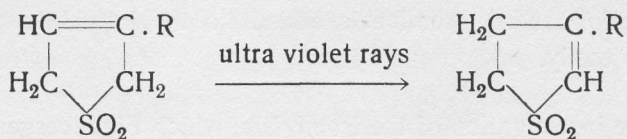
Since neither the sulphone of butadiene nor that of 2,3-dimethyl butadiene-1,3 show isomerism under the same circumstances as the isoprene sulphone, it is obvious that, in case of isomerism, only one hydrogen atom of the doubly-bound carbon atoms in the butadiene sulphone, has to be substituted. This is indeed the case; with the sulphones of 2-phenyl and 2-tertiary butyl butadiene, that fulfill these conditions, isomerism appears.

From these facts we may conclude, that *with sulphones of butadienes isomerism can occur, when one of the doubly-bound carbon atoms bears an alkyl or aryl group, and the other a hydrogen atom.*

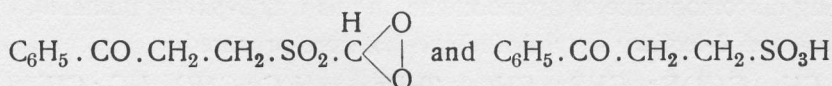
Eigenberger's opinion, that the isomerism is due to a cis-trans configuration on the double bond, is *erroneous*. Eigenberger gives the following formulas for the two isoprene sulphones:



Oxidation with ozone showed, that the difference in constitution is caused by a *shifting of the double bond*.



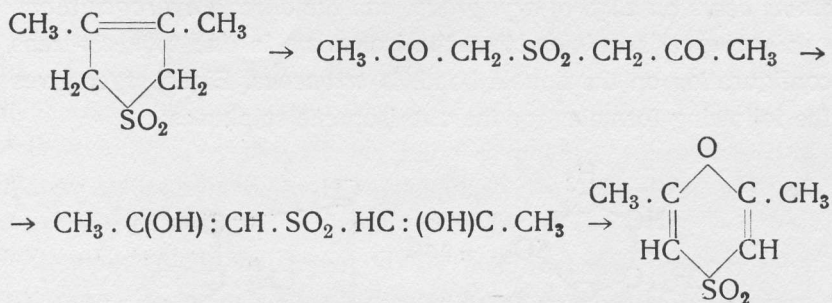
The products, resulting from this breaking up process were isolated in the case of the isomeride of the sulphone of 2-phenyl butadiene-1,3, viz. the β -benzoyl ethyl sulphonyl-iso-formic acid and β -propiophenone sulphonic acid:



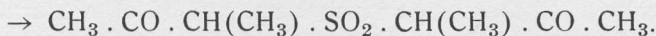
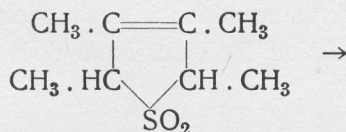
Their formation can easily be explained from the formula given. Amongst the oxidation products of the isomeric tertiary butyl derivative only trimethyl acetyl methane sulphonic acid was isolated as baryum salt.



With the different representatives this breaking up of the sulphones by means of ozone leads to very divergent final products, which are characteristic for the structure of the sulphones. Thus, from the sulphone of 2,3-dimethyl butadiene a product arises with an internal ether function, the formation of which takes place by removal of water from the enol form of the diketone:

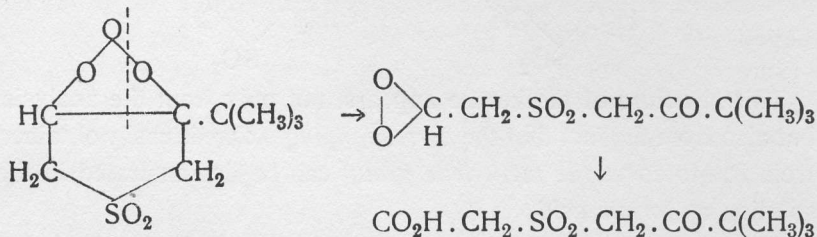


With the sulphones from 1,2,3,4-tetramethyl and 2,3-diphenyl butadiene-1,3 the corresponding diketones are formed. Here enolisation and formation of a cycle do not take place:



The same applies to the sulphone from 2,3-diphenyl butadiene-1,3. The oxidation of the three above mentioned sulphones was carried out in *acetic acid* as a solvent.

The *sulphones of 2-tertiary butyl and 2-phenyl butadiene-1,3* which, with ozone, do not yield pure products in acetic acid, have been treated with ozone in a solution of an indifferent solvent, to which water had been added. The ozonide, formed in the first instance, is then split up into products, which still contain active oxygen. In this way from the sulphones of 2-tertiary butyl and 2-phenyl butadiene-1,3, products were obtained, possessing strong oxidizing as well as acid properties. They are *isomerides of carboxylic acids and have, therefore, been called iso-carboxylic acids*. With alkalis or amines they change into the salts of the normal acids.



The *normal acids* can be made from the iso-carboxylic acids, by transmuting the latter into the salts of the normal acids with alkali; liberated from the salts by means of sulphuric acid, they can be gained from the solution by means of extraction with ether.

An easier method to obtain them, is heating the iso-carboxylic acids in acetone solution with a little water.

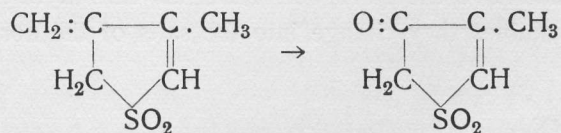
The velocity of the transition of the iso-carboxylic acid from the tertiary butyl derivative into the normal acid has been measured; it is a *mono-molecular process*.

With *diazomethane* the normal acid easily yields the methyl ester; the iso-carboxylic acid on the other hand does not react with the diazo compound.

On account of the comparatively easy method of preparation of the butadiene, the *sulphone of 2,3-dimethyl butadiene-1,3* has been examined most closely. Both *stereo-isomeric dihydroxy compounds*, viz. the *cis-* and *trans-*derivatives, were prepared; the former, by means of oxidation of the sulphone with potassium permanganate, the latter by hydrolysis of the dibromide. With acetic acid anhydride and strong sulphuric acid, these easily yield the *corresponding diacetoxy compounds*.

Whereas the dibromide is hydrolyzed by boiling water (into the *trans-dihydroxy product*), *two molecules of hydrogen bromide are split off under the influence of alkali*.

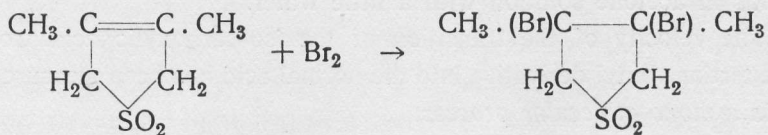
The *structure of the resulting product* is proved by the oxidation, by means of ozone, to a ketone:



This structure of the ketone appears, not only from the analysis, but also from the fact that the *corresponding oxime* is easily obtained from it. Moreover the *methylene group* can be demonstrated in the solution as *formic acid*.

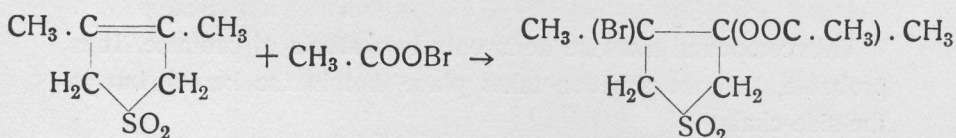
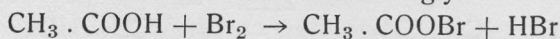
A *dibromide* was obtained from the *methylene derivative* by treating it with bromine. The two bromine atoms are fixed in the side-chain.

The *dibromide of the sulphone of 2,3-dimethyl butadiene-1,3* is formed in practically quantitative yield, if the addition of bromine is carried out in an indifferent solvent:

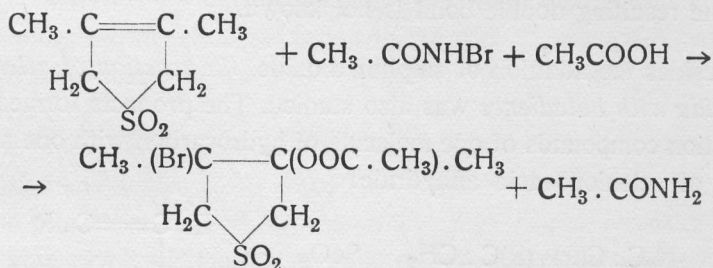


If, however, *the addition takes place in acetic acid as a solvent*, the dibromide gives a yield of only 80 %. This lower yield of dibromide is due to the *occurrence of a by-reaction*, which appears still more strongly, if chlorine instead of bromine is added to the double bond.

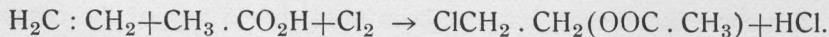
It appeared, namely, that solutions of bromine or chlorine in acetic acid act partly as acetyl hypobromite or acetyl hypochlorite respectively. This is fixed to the double bond, so that the yield of dibromide or dichloride is reduced accordingly.



For *identification* purposes the same products have been prepared in an other way. A solution of acetyl hypobromite can be obtained by treating acetbromoamide with acetic acid. In the presence of a double bond, addition of this product takes place, in such a way that the bromine atom is bound to one carbon atom, the acetate group to the other.



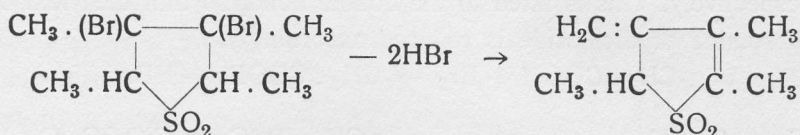
This unknown reaction of chlorine dissolved in acetic acid, has also been applied to the simplest unsaturated compound, viz. *ethylene*. Here, besides dichloroethylene, a considerable quantity of β -chloroethyl acetate was obtained:



From the facts stated above, the conclusion may be drawn, *that*

solutions of bromine and chlorine in acetic acid react upon products with a double bond partly as solutions of acetyl hypobromite and acetyl hypochlorite.

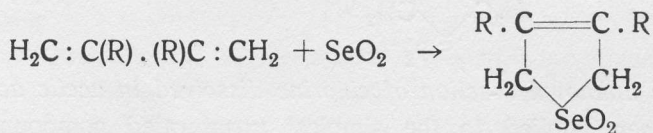
The dibromide of the sulphone of 1,2,3,4-tetramethyl butadiene-1,3, when heated with alkali, loses two molecules of hydrogen bromide. Probably a reaction takes place analogous to that with the same derivative of the sulphone of 2,3-dimethyl butadiene-1,3.



This compound likewise adds only two atoms of bromine. It is probable, that the addition takes place, not in the kernel, but in the side-chain.

Of the sulphone of 2-phenyl butadiene-1,3 the dihydroxy derivative was prepared by means of oxidation with potassium permanganate. The corresponding diacetyl compound has not been obtained. By treatment with acetic acid anhydride and strong sulphuric acid a monoacetoxy product is formed. The other hydroxyl group combines with a hydrogen atom to form water; the place of the resulting double bond is not known.

Besides the addition of sulphur dioxide, the reaction of selenium dioxide with butadienes was also studied. The products formed are addition compounds of one molecule of hydrocarbon with one molecule of selenious acid anhydride:



The selenones are well crystallized compounds. Formation of polymerisation products, as with the reaction of sulphur dioxide with some butadienes, has not been observed in any of the cases of addition of selenium dioxide. The selenones obtained are, how-

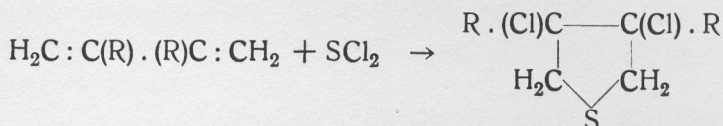
ever, not very stable. The compound that can be preserved best, is that obtained from 2,3-ditertiary butyl butadiene-1,3. This selenone gives with sulphur dioxide a reaction product, the structure of which could not yet be explained. Contrary to the selenones, this product is very stable and durable.

The addition of selenium dioxide was always carried out at ordinary temperature; it appears that alkyl groups have a great influence on the reaction. An explanation for this has been given.

Besides the addition of sulphur dioxide and selenium dioxide, the reaction of *sulphur dichloride with some butadienes* was studied.

As compounds with conjugated double bonds, butadiene, isoprene and 2,3-dimethyl butadiene-1,3 were taken. The addition of sulphur dichloride takes a different course from that of sulphur and selenium dioxide.

With *isoprene and 2,3-dimethyl butadiene-1,3* the course of the reaction is the same as in the case of ethylene.



The *thio-ether of 2,3-dimethyl butadiene* has been obtained in a pure state; by means of oxidation to the well-known 3,4-dimethyl-3,4-dichloro-thiacyclopentane-1,1-dioxide, the structure has been ascertained.

The thio-ether function has been proved by the addition of corrosive sublimate.

The *thio-ether derived from isoprene* could not be obtained in a pure state. The *sublimate compound and the oxidation product*, the 3-methyl-3,4-dichloro-thiacyclopentane-1,1-dioxide, have been obtained in a pure state.

Of *butadiene* the only product that was obtained pure, is butadiene tetrachloride. Formation of a thio-ether was not observed.

For the feeble inclination towards cyclisation with butadiene, a similar explanation has been given as in the case of the preparation of the selenones.