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OZONOLYSIS BY MICROWAVE DISCHARGE OF OXYGEN OF NAPHTHALENE ADSORBED ON FLORISIL

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SUMMARY Microwave discharge of O_2 produces $O(^3P)$ atoms which form O_3 on florisil surface. Reaction with adsorbed naphthalene results in o-formylcinnamaldehydes as the main product.

We have recently shown[1] that microwave discharge of oxygen may be used as an alternative method for ozonations of organic compounds, replacing in some cases the conventional method which utilizes high voltage electric discharge of oxygen.

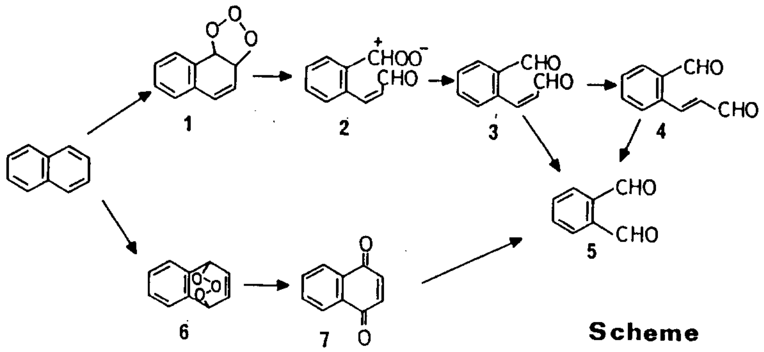
The new method consists of discharging by microwaves (2450 MHz) a mixture of helium and oxygen (85:15) at 2 torr in a flow system, and passing the discharged gases over silica gel or florisil preadsorbed with the substrate (2% w/w), ca. -78°C. The $O(^3P)$ atoms formed by discharge combine on the surface of the adsorbent with oxygen molecules forming ozone which slowly accumulates on the adsorbent.[1] By this technique, ozone is formed in low concentration in situ, and might thus be used i.a. for selective ozonation of one of several double bonds in polyunsaturated or aromatic molecules.

We attempted to utilize the microwave method for oxidative cleavage of only one of the naphthalene double bonds, which on conventional ozonolysis results in a cleavage of two double bonds in one of the benzene rings.[2,3] Thus it was previously reported that ozonolysis of naphthalene in the presence of water, followed by reduction results in phtaldialdehyde. This compound was also obtained as the only product after passing ozone at -78°C, through florisil preadsorbed with naphthalene for 5 minutes.[4,5]

The microwave discharge ozonation was also performed on florisil preadsorbed with naphthalene (prepared by evaporation to dryness of a chloroform solution of naphthalene in the presence of florisil on a rotatory evaporator). The reaction was performed by passing a stream of discharged He/O_2 mixture over stirred florisil at -78°C. After 2 hrs reaction, ca. 30% of naphthalene was converted to cis- and trans-o-formylcinnamaldehyde 3 and 4 (40% and 30%, respectively), phtaldialdehyde 5 (20%), and 1,4-naphthoquinone 7 (<5%) (Scheme).

Aldehydes 4[6] and 5 were purified by partial high vacuum sublimation and naphthoquinone 7 by a preparative TLC, and were identified by comparison with authentic samples. The structure of the cis-dialdehyde 3, which could not be isolated in a pure form (because of its fast isomerization to its trans-dialdehyde-4), was deduced from the characteristic NMR spectrum (aldehydic

H: δ 10.17s and 9.70d, J=8.2 Hz, *cis*-vinylic H: δ 8.12d, J=11.5 and 6.32dd, J=8.2, 11.5 Hz).



Scheme

It may, thus, be assumed that the major ozonation pathway involves a primary formation of molozonide 1 which rearranges to aldehydocarbonyloxide 2. The latter decomposes on the solid adsorbent (probably hydrolitically due to the adsorbed water) to the *cis*-dialdehyde 3. Analogous formation of aldehydes without the intermediacy of ozonides has previously been observed by us on phenylethylenes adsorbed on silica gel or florisil.[5] *Cis*-dialdehyde 3 is further oxidized to phtaldialdehyde 5 directly, or after isomerization to *trans*-dialdehyde 4. A minor ozonation pathway involves 1,4-ozone addition, forming an endo-trioxide 6, the precursor of naphthoquinone 7.

The above results induced us to look for these products also on conventional ozonations. Accordingly, we passed ozone (produced in Welsbach ozonizer) through a thin layer of florisil containing naphthalene for ca. 30-60 seconds, and obtained a low conversion to phtaldialdehyde 5 and *trans*-*o*-formylcinnamaldehyde 4.[5] The other two microwave ozonation products, 3 and 7 were formed only in traces. As a homogenous concentration of ozone on the support could not be attained in such a short time, the conversions were erratic, ranging from 0.5-10%. Longer reaction periods led, however, to the complete disappearance of 4.

It may be concluded that ozonation by microwave discharge is a potentially useful method for a partial oxidative cleavage of polycyclic aromatic compounds.

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