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PYROLYSIS OF NAPHTH[1,8-cd]-1,2-OXATHIOLE-2,2-DIOXIDE [1]

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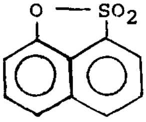
We have reported the mass spectra and pyrolysis results of several aromatic compounds [2]. As part of the project, naphth[1,8 cd]-1,2-oxathiole-2,2-dioxide (1) has been pyrolyzed in a stream of nitrogen by sublimation into a pyrolysis zone constructed from 24 mm Vicor tubing. The heating element was a coil which was made out of 120 cm of 20 gauge chromel wire. It is 11 mm in diameter and 80 mm in length and was located inside the pyrolysis tube. A series of cold traps condensed the products emerging from the pyrolysis zone.



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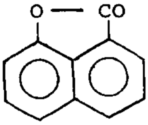

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When 1 was pyrolyzed at 650° with nitrogen as the carrier gas and at a pressure of 3.0-3.5 mm for the system, indene (0.5%), naphthalene (0.3%), 1-naphthol (7.5%), and naphtho[1,8-bc] furan-2-one (2, 2.1%) were the major products. The yield of 1-naphthol increased to 22% when methanol was introduced into the nitrogen stream before it entered the pyrolysis zone.

The formation of 1-naphtol can be rationalized in terms of the loss of SO_2 from 1 to form an intermediate which abstracts two hydrogen atoms.

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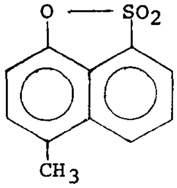
The yield of 1-naphthol increased by a factor of three when methanol, a hydrogen source, was present. Naphthalene and indene could be formed by further loss of CO from the intermediate and degradation to acetylenes, followed by recombination [3]. Compound 1 fragments by loss of SO_2 followed by CO in the mass spectrometer, upon electron impact [m/e (rel. intensity, 70 eV): 206(74, mol. ion), 142(74), 114(100)].

We were intrigued by the presence of lactone 2; apparently the intermediate formed by loss of SO_2 was also trapped with CO. We substituted carbon monoxide for nitrogen as the carrier gas, using a pyrolysis temperature of 650° and a carbon-monoxide pressure of 200 mm. The yield of 2 increased to 79-95%, based on quantitative glpc determinations on five experiments; yields of 65-76% were obtained from isolation of pure material.

Pyrolysis of 6-methylnaphth[1,8-cd]-1,2-oxathiole-2,2-dioxide (3) at 680° in nitrogen at 3.5 mm gave a yield of 6.9% of a mixture of 4-methyl- and 5-methyl-1-naphthol (4 and 5). The yield was increased to 24% when methanol was added to the nitrogen stream. The ratio of 4-methyl-to 5-methyl-1-naphthol was 1 to 1.1. Also, in the pyrolysis of 3 a yield of 0.9% of a mixture of the 6-methyl and 5-methyl derivatives of 2 was obtained. When carbon monoxide was used as the carrier gas, the yield of this mixture increased to 70%; the ratio of 6-methyl to 5-methyl was 1 to 1.2.



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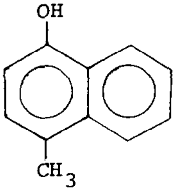

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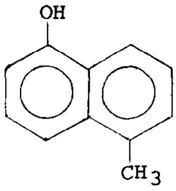

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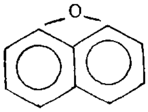
In order to explain the data obtained from the pyrolyses of 1 and 3, the formation of an intermediate or transition state in which positions 1 and 8 become equivalent must be invoked. Positions 1 and 8 could become equivalent via peri-monooxynaphthalene (6) [4,5]. One possibility is rearrangement of 1 to 1,8-naphthalene sulfite (7) from which SO_2 can be lost



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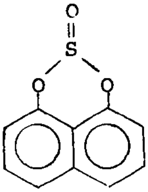

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including the ring oxygen at position 8 as well as the one at position 1. However, pyrolysis of 7 under our conditions did not give results similar to those obtained from 1.

Trapping of CO has been reported previously, but high pressures and/or inorganic catalysts were required. For example, o-cresol and dicobalt octacarbonyl in a stainless-steel tube with CO at 300° and 1,000 atm gave a 14% yield of 2(3H)-benzofuranone [6]. Our conditions were much less severe, and high yields were obtained.

Compound 1 was prepared by a published procedure [7]. Compound 2 was identified by elemental analysis, spectral data, and its mp 103-105° (lit.[8] mp 99-101); its methyl ester was prepared, mp 63.5-65° (lit.[8] mp 64-65°). Compound 3 was prepared by the procedure of Schetty [9]. The 4-methyl- and 5-methyl-1-naphthol (4 and 5) mixture was observed by nmr (CCl_4): δ2.51 (s, 3H) and δ2.43(s, 3H). The mixture of the 6- and 5-methyl derivatives of 2 was studied in the form a mixture of methyl 4- and 5-methyl-8-hydroxy-1-naphthanoate; nmr (CCl_4): CO_2CH_3 δ3.98 (s, 6H), C-CH_3 δ2.63 (s, 3H), and C-CH_3 δ2.55 (s, 3H). Compound 7 was prepared by a known procedure [10].

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1. This work was supported in part by a grant from the National Institutes of Health.
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