liquid, b.p. 70–73°/7 mm., was collected as the sole product of the reaction; yield, 12.5 g. (72%). Almost identical results were obtained when free *trans*-3-hexenedioic acid was pyrolyzed at 280 to 285°. The pyrolysis product was a colorless liquid, b.p. 186–188°/740 mm. (reported[13] b.p. 188°), with a disagreeable odor typical of $C_5$ fatty acids; it was found to be a monobasic olefinic acid (neut. equiv.: calcd. 100; found: 99). The infrared spectrum showed a terminal double bond and suggested that the compound was 4-pentenoic acid (IV). This structure was verified by ozonolysis of a sample in acetic acid solution; the products after decomposition of the ozonide were found to be formaldehyde (identified as its dimedone derivative, m.p. 191–192°) and β-formylpropionic acid (V), identified as the 2,4-dinitrophenylhydrazone, m.p. 203–204° dec. (reported[14] m.p. 201°). Further substantiating the identity of the pyrolysis product were its refractive index, $n_D^{25}$ 1.4279 (reported[15] $n_D^{26}$ 1.4274), and the *p*-bromophenacyl ester, m.p. 57–58° (reported[15] m.p. 57–58°).

*Pyrolysis of cis-3-hexenedioic acid* (X). When a mixture of 5 g. of *cis*-3-hexenedioic acid (X) and 0.25 g. of barium hydroxide was heated at about 275 to 285° in a Claisen distilling flask, the sole product in the distillate was 4-pentenoic acid, b.p. 185–188°; yield, 2.3 g. (66%); $n_D^{25}$ 1.4275. This product was identical in all respects (infrared spectrum, melting point of *p*-bromophenacyl ester) with the 4-pentenoic acid obtained from *trans*-3-hexenedioic acid, and there was no evidence that any neutral products were obtained from the pyrolysis reaction. Nearly identical results were obtained when free *cis*-3-hexenedioic acid was pyrolyzed.

*Pyrolysis of calcium acrylate.* A mixture of 50 g. of calcium acrylate and 80 g. of clean sand was heated in a flask fitted with a gooseneck and condenser with a graphite bath at about 450 to 500°. The mixture darkened and frothed, and a small amount (*ca.* 5 g.) of a dark oil gradually distilled. After being dried with anhydrous magnesium sulfate, the pyrolyzate was distilled and was found to consist of a complex mixture from which no pure compounds were isolated. There was only a trace of material boiling in the range of 130–140° (reported[3] b.p. for 3-cyclopentenone, 133–135°), and it had $n_D^{23}$ 1.4371 (reported[2] for 3-cyclopentenone, $n_D^{20}$ 1.4536) and was not the desired product. Variations in the method of carrying out the pyrolysis failed to effect formation of any detectable amounts of 3-cyclopenten-1-one.

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## Ozonolysis of Methylnaphthalenes

R. H. Callighan[1] and M. H. Wilt[2]

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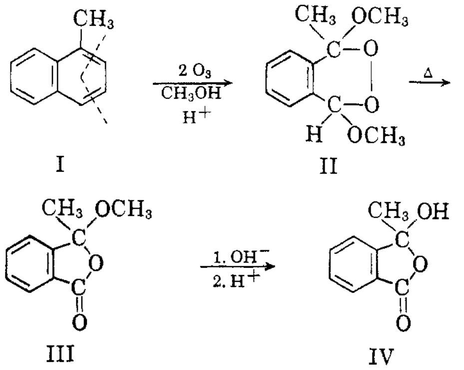
More than fifty years ago, Harries and Weiss[3] reported the isolation of a diozonide from the ozonolysis of naphthalene in chloroform. Investigators have continued to assume that the ozonide of naphthalene is a diozonide because two moles of ozone per mole of naphthalene is absorbed. Examination of the Criegee mechanism[4] for ozonolysis leads one to expect that the naphthalene ring would be cleaved at the 1,2- and 3,4-bonds to yield a monoozonide with two carbons fewer than in naphthalene. Bailey[5] has presented good evidence for the existence of a monoozonide of naphthalene; however, the product was too unstable to analyze and exploded if allowed to dry in chunks. Bailey observed that in methanol, the zwitterion reacted with the solvent to give a 94% yield of a stable crystalline peroxide. It seemed of interest, therefore, to determine whether the ozonolysis of methyl naphthalenes would proceed in a similar manner.

Ozonolysis of 1-methylnaphthalene (I) in methanol at −70° followed by partial evaporation, addition of a few drops of concentrated hydrochloric acid, and recooling to −70° for about sixteen hours gave a 5% yield of a colorless crystalline peroxide. The material was assigned the structure of 3,6-dimethoxy-3-methyl-4,5-benzo-1,2-dioxacyclohexane (II) on the basis of its infrared spectrum and elemental analysis. All attempts to increase the yield of this material were unsuccessful.



During ozonolysis, two molecular equivalents of ozone were absorbed. Furthermore, ozone attacked only in the methylated ring since alkaline permanganate oxidation of the ozonolysis reaction mixture gave only phthalic and no hemimellitic acid. The colorless solution that resulted after ozonolysis evolved oxygen when treated with lead tetraacetate. This reaction is characteristic of hydroperoxides.[6] The hydroperoxide could be destroyed by refluxing the methanolic solution for approximately sixty-eight hours. Evaporation of the solvent led to isolation of a neutral nonperoxidic oil in high

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(3) C. Harries and V. Weiss, *Ann.*, **343**, 336 (1905).

(4) R. Criegee, *Record Chem. Progr.*, **18**, No. 2, 111 (1957).

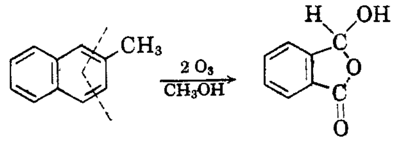
(5) P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957).

(6) R. Criegee *et al.*, *Chem. Ber.*, **72**, 1799 (1939).

yield. Although this oil had a saponification equivalent very close to that of methyl *o*-acetylbenzoate (III), only a 23% yield of crude *o*-acetylbenzoic acid (IV) could be obtained by saponification of the oil. Vacuum distillation of the neutral oil resulted in considerable decomposition or polymerization, but methyl *o*-acetylbenzoate was obtained in 48% yield. Saponification of the distilled methyl ester gave an 80% yield of crude *o*-acetylbenzoic acid. Analysis of the distilled ester by gas chromatography indicated that probably at least three components were present in the oil. In contrast, saponification of an authentic sample of III gave a 91% yield of pure IV. Elution chromatography of the neutral oil confirmed the suspicion that several components were present; however, separation into pure materials was not obtained. Chromic acid oxidation of 1-methylnaphthalene is reported to give *o*-acetylbenzoic acid as the major product, although numerous side reactions occur.[7]

Ozonolysis of 1-methylnaphthalene in methanol at low temperature (−40°) followed by reduction of the active-oxygen-containing products with potassium iodide also failed to give a single product in good yield. In this reaction sequence, the expected product was *o*-acetylbenzaldehyde. A search of the literature showed that of the three possible isomeric acetylaldehydes, only *p*-acetylbenzaldehyde is known. The known keto aldehyde was reported by Detweiler and Amstutz[8] to be very unstable. The reduction product obtained from ozonolysis of I was a dark red, viscous oil. Although the material appeared to decompose gradually at room temperature, it decomposed rapidly to a tar-like material when heated. Attempts to form derivatives gave either no reaction or mixtures that could not be separated. A Clemmensen reduction also did not lead to any identifiable product. The crude product reacted with the skin to produce a blue coloration. A blue color was also formed with glycine, and various hues of blue were developed with the following amino acids: DL-lysine, L-asparagine, DL-threonine, DL-isoleucine, β-alanine, L-tryptophane, DL-norvaline, DL-norleucine, and DL-methionine. No color reaction was observed with L-proline, L-cystine, and DL-tyrosine. Although ninhydrin reacted with all of the amino acids listed, the hue with a given amino acid was different from that produced by the unknown oil.

The ozonolysis of 2-methylnaphthalene (V) proceeds similarly to that of naphthalene, but isolation of pure compounds in good yield is much more difficult. Ozonolysis of V in methanol at −40° resulted in absorption of two molecular equivalents of ozone. All attempts to isolate a crystalline cyclic peroxide were unsuccessful. Evaporation of the solvent under reduced pressure, followed by acid hydrolysis of the resulting peroxidic oil, gave a 60% yield of very crude phthalaldehydic acid (VI). The crystallized acid was identified as VI by its melting point, neutral equivalent, and infrared spectrum.



V VI

It thus appears that the ozonolysis of methylnaphthalenes is much more complex than ozonolysis of the parent compound, naphthalene. All attempts to isolate a single compound in high yield from the ozonolysis of I or V were unsuccessful.

## EXPERIMENTAL

The 1- and 2-methylnaphthalenes used in this work were commercial materials, which were estimated to be of 99 to 100% purity. The methanol was A.C.S. reagent grade material. All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord Model 137 infrared spectrophotometer fitted with a sodium chloride prism. Elemental analyses were performed by the Mellon Institute Microanalytical Laboratory. Other reagents mentioned were of the purest quality obtainable. The ozonator and accessory equipment have been described previously.[9]

*3,6-Dimethoxy-3-methyl-4,5-benzo-1,2-dioxacyclohexane* (II). A solution of 1-methylnaphthalene (14.2 g., 0.1 mole) in 200 ml. of methanol was cooled to −70°, and then 2.4 mole-equivalents (2.3 wt. % at 1.1 mmoles/min.) of ozone was passed into the solution. The blue color of the solution was discharged by flushing with oxygen, and the total solution was found to contain 142 mmoles of active oxygen (theory = 200 mmoles). The solution gave a positive test for hydroperoxide. The solution was allowed to come to room temperature and was then evaporated to one half the original volume with an air blast. Two drops of concd. hydrochloric acid were added, and the solution was again cooled to −70° and kept at this temperature overnight (16 hr.). Needle-like crystals precipitated, which were removed by filtration and dried in a vacuum desiccator. A 1.0-g. yield (4.8%) of crude 3,6-dimethoxy-3-methyl-4,5-benzo-1,2-dioxacyclohexane, which melted at 99–110°, was obtained. One recrystallization from ethyl acetate–*n*-heptane gave 0.6 g. (2.9% yield) of pure material melting at 124–126°. The infrared spectrum showed the absence of hydroxyl and carbonyl bands, but showed the presence of an ether band at 9.2 μ and a band at 7.2 μ which seems to be typical of methyl ethers.

*Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 62.80; H, 6.72; $OCH_3$, 29.52. Found: C, 62.79; H, 6.52; $OCH_3$, 29.22.

*Methyl o-acetylbenzoate* (III). A solution of 1-methylnaphthalene (0.1 mole) in 200 ml. of methanol was treated with 2.0 mole-equivalents of ozone at room temperature (+30°). A small amount of ozone escaped unabsorbed. After flushing with oxygen, the colorless solution was transferred into a 500-ml. round-bottom flask, 1 ml. of pyridine

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(7) G. Bendz and A. Thalen, *Arkiv Kemi*, **14**, 519 (1959).

(8) W. K. Detweiler and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2882 (1950).

(9) R. H. Callighan, M. F. Tarker, Jr., and M. H. Wilt, *J. Org. Chem.*, **25**, 820 (1960).

was added,[10] and the mixture was allowed to reflux for 4 hr. The solution, after refluxing, gave a positive test for active oxygen with potassium iodide–starch test paper. The methanol was removed by evaporation at reduced pressure in a flash evaporator, and a light yellow-green oil with a pungent odor was obtained. Distillation of the crude oil (18.2 g.) under vacuum in a spinning-band column yielded 8.6 g. of light yellow oil boiling at 139–146° (12 mm.). The total yield of distilled methyl *o*-acetylbenzoate was 48%. The infrared spectrum indicates that this keto ester exists mainly in the cyclic lactol form.

*Anal.* Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.64; sapon. equiv., 178. Found: C, 67.21, 67.29; H, 5.38, 5.55; sapon. equiv., 178.

*o-Acetylbenzoic acid* (IV). A sample of distilled methyl *o*-acetylbenzoate (3.0 g., 0.0169 mole) was weighed into a 50-ml. round-bottom flask, sodium hydroxide (1.0 g., 0.025 mole) in 20 ml. of water was added, and the mixture refluxed for 30 min. Upon cooling, the now black solution was acidified with concentrated hydrochloric acid. A red-yellow oil separated, which after crystallizing overnight was filtered, washed with water, and dried in a vacuum desiccator. The yield of crude *o*-acetylbenzoic acid, which melted at 84–104° and had a neutral equivalent of 174, was 2.2 g. (80%). Pure *o*-acetylbenzoic acid is reported to melt at 114–115°[7] and to have a neutral equivalent of 164. The crude product was identified by comparison of its infrared spectrum with that of an authentic sample obtained from the Aldrich Chemical Co.

*Attempted preparation of o-acetylbenzaldehyde.* A solution of 1-methylnaphthalene (0.1 mole) in 200 ml. of methanol was cooled to −40°, and then 2.0 mole-equivalents of ozone were passed through the solution. The ozone uptake was not quantitative. After flushing with oxygen, the total solution was found to contain 164 mmoles of active oxygen (theory = 200 mmoles). The cold solution was transferred into a 500-ml. Erlenmeyer flask and recooled to −40°. Solid sodium iodide (60 g., 0.4 mole) and 5 ml. of glacial acetic acid were added slowly with stirring. An exothermic reaction occurred, and the solution was warmed to 0°. After about 1 hr., the solution was allowed to warm to room temperature and the liberated iodine reduced with 20% aqueous sodium thiosulfate solution (about 200 ml.). The methanol was then removed by evaporation on a steam bath under an air blast. The resulting aqueous solution was extracted with three 50-ml. portions of ether, and the combined extracts were dried (sodium sulfate) and evaporated under reduced pressure in a flash evaporator. Evaporation yielded 10.7 g. of orange-red oil. The infrared spectrum showed a hydroxyl band at 2.9 $\mu$ and a doublet carbonyl band at 5.7 $\mu$ and 6.0 $\mu$.

Although the viscous oil appeared to decompose gradually at room temperature, it decomposed rapidly to a tar-like material when heated. Attempts to form derivatives gave either no reaction or mixtures that could not be separated. A Clemmensen reduction also did not lead to any identifiable product.

*Phthalaldehydic acid* (VI). A suspension of 2-methylnaphthalene (14.2 g., 0.1 mole) in 100 ml. of methanol was treated with 2.0 mole-equivalents of ozone at a temperature of −40°. The ozone uptake was not quantitative, and the reaction vessel was shaken intermittently to allow undissolved 2-methylnaphthalene to come into more intimate contact with the gas stream. After flushing with oxygen, the solution was transferred into a 500-ml. round-bottom flask and evaporated under reduced pressure until most of the methanol had been removed. At this stage, 30 ml. of distilled water and 20 ml. of glacial acetic acid were added, and the mixture was allowed to reflux for 1 hr. After the solution was refluxed, it gave a negative test for peroxides with potassium iodide–starch test paper. The water and acetic acid were removed by evaporation under reduced pressure, and the residual oil was treated with 100 ml. of 7% aqueous sodium bicarbonate solution and warmed on a steam bath for 30 min. After cooling, insoluble neutral material was removed by extraction with ether. Upon acidification of the bicarbonate solution with concentrated hydrochloric acid, a viscous, red oil separated. The oil was extracted with ether (100 ml.), and the ether extract was evaporated to dryness to yield 9.0 g. (60% yield) of very crude phthalaldehydic acid, which was identified by its infrared spectrum. Recrystallization from benzene yielded 0.6 g. (4% yield) of white solids that melted at 89–94° and had a neutral equivalent of 150. Pure phthalaldehydic acid reportedly melts at 97°[11] and has a neutral equivalent of 150. The infrared spectrum of the crystalline material was identical with that of an authentic sample obtained from the Dow Chemical Co.

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[11] D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

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## Deboronation: Formation of Phenylboronic Anhydride from Diphenyl Hydroxyborane in the Presence of Amides[1]

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The deboronation of aryl groups in aryldihydroxyboranes and diaryl hydroxyboranes has been known for many years.[3,4] Normally the deboronating agent is of a kind which may generally be considered an oxidizing agent (*e.g.*, hydrogen peroxide bromine or chlorine), and since the boron-containing product is usually in an apparently higher oxidation state (*viz.* boric acid from phenyl dihydroxyborane, or phenyl dihydroxyborane from diphenyl hydroxyborane than before the reaction, such processes are frequently regarded as oxidations. During the past decade, Kuivila and his students[5]) have studied the aryl dihydroxyboranes and their deboronations quite extensively from this viewpoint.

We have recently found evidence that a deboronation of an aryl group in diphenyl hydroxyborane can occur under clearly nonoxidizing conditions when the compound is allowed to reflux in an or-

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