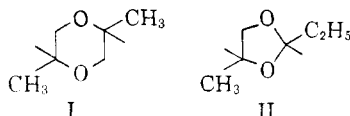


rolysis of polypropylene oxide in the presence of *p*-toluenesulfonic acid produced propionaldehyde, propionic and acrylic acids, and dimethyldioxane. Dr. R. K. Summerbell has suggested to us² that the properties we reported for the latter substance indicated it to be the isomeric 2-ethyl-4-methyldioxolane. We have therefore reinvestigated the identity of this pyrolysis fraction and find it does indeed contain considerable quantities of 2-ethyl-4-methyldioxolane (II), as well as an isomer, probably *trans*-2,5-dimethyldioxane (I).



The presence of II was proven by the acid hydrolysis of the pyrolysis product in the presence of 2,4-dinitrophenylhydrazine to produce propionaldehyde 2,4-dinitrophenylhydrazone, by infrared spectra, by vapor chromatography,³ and by nuclear magnetic resonance.⁴

The latter three measurements also indicated the presence of an isomer, probably *trans*-2,5-dimethyldioxane, in roughly equal amounts.

Since II is readily prepared by acid-catalyzed condensation of propylene glycol with propionaldehyde, it is not clear whether this compound is a direct product of pyrolysis or is formed from the glycol and aldehyde as a secondary product.

EXPERIMENTAL

Pyrolyses. A 29-g. sample of polypropylene oxide and 0.3 g. of *p*-toluene sulfonic acid were heated together in a sand bath at 270–330° to give 25.5 g. of yellow distillate and 2 g. of black residue. Redistillation through a 6-inch Vigreux column gave 8.5 g., b.p. 51–87°; 10 g., b.p. 87–113° and 3.0 g., b.p. 113–165°. Two redistillations of the main fraction gave three fractions corresponding to dimer, 0.5 g., b.p. 117–120°, n_D^{25} 1.4073; 2.5 g., b.p. 121–123°, n_D^{25} 1.4088; 1.5 g., b.p. 123–128°, n_D^{25} 1.4102.

A similar pyrolysis of 114 g. of polypropylene oxide (Ucon "2025," Carbide Chemicals Corporation) gave the following dimer fractions, after three redistillations: 1.5 g., b.p. 117–119°, n_D^{25} 1.4090; 2.0 g., b.p. 119–120°, n_D^{25} 1.4112; 2.0 g., b.p. 120–122°, n_D^{25} 1.4130; 1.5 g., b.p. 122–125°, n_D^{25} 1.4141.

The infrared spectra of all seven dimer samples were almost identical, except for changes in relative intensity of bands, and all were very similar to the spectra reported earlier by St. Pierre.¹

The infrared spectrum of 2-ethyl-4-methyldioxolane, b.p. 117.5°, n_D^{25} 1.4048, prepared by condensation of propionaldehyde and propylene glycol,³ was similar to the dimer fractions, except for the absence of bands at 7.86 μ and 11.86 μ . These are the only two major bands for *trans*-2,5-dimethyldioxane⁵ not present also in the dioxolane.

(2) Private communication.

(3) Courtesy of Dr. L. E. St. Pierre, Research Laboratories, General Electric Company, Schenectady, N. Y.

(4) Courtesy of Dr. J. D. Roberts, California Institute of Technology, Pasadena, Calif.

(5) Samples of *trans*-2,5-dimethyldioxane and the mixed *cis-trans* isomers were kindly supplied by R. K. Summerbell and D. Dalton, Northwestern University.

The strong band in *cis*-2,5-dimethyldioxane at 8.23 μ is almost entirely absent in the pyrolysis product. The bands at 7.1, 9.65, 10.75, and 11.03 μ in the dioxolane are considerably weaker in pyrolysis product fractions boiling at 122–125° than those boiling at 117–119°. A rough approximation from band intensities would suggest that the main components of the pyrolysis are 2-ethyl-4-methyl dioxolane and *trans*-2,5-dimethyldioxane in roughly equal amounts.

The fact that the dimer fractions are not pure dioxolane is further supported by the spread in boiling point and refractive index.⁶ Assuming a two component mixture and a linear relation between composition and refractive index, the material from the second pyrolysis would be about 40% dioxolane and 60% dioxane. From this same material, vapor chromatography³ gave a fraction identified as the dioxolane (55%) and another fraction, probably the dioxane (45%).

A comparison of the nuclear magnetic resonance spectrum⁴ of the pyrolysis product with the markedly different spectra of 2-ethyl-4-methyldioxolane and *trans*-2,5-dimethyldioxane was entirely consistent with the conclusion that the pyrolysis mixture contained roughly equal amounts of these isomers.

It was also noted that the synthetic dioxolane crystallized in a Dry Ice-acetone bath whereas none of the dimer fractions did so.

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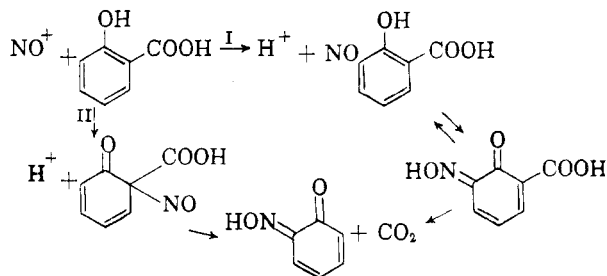
(6) E. Augdahl, *Acta Chem. Scand.*, 9, 1237 (1955) has reported *trans*-2,5-dimethyldioxane, b.p. 121.5°, n_D^{25} 1.4147.

Nitrosodecarboxylation

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The addition of sodium nitrite to an aqueous ethanolic solution of salicylic acid causes an immediate and rapid evolution of carbon dioxide; some 2-nitrophenol can be distilled from the resulting solution. This decarboxylation could conceivably occur by either of the following reaction paths:



The resulting *ortho*-quinone monoxime or 2-nitrosophenol would then be oxidized by excess nitrite to the 2-nitrophenol. From the nature of the product recovered, it is not possible to differentiate between these two routes. Similarly, the formation of 2-nitro-4-methylphenol from sodium nitrite and 5-methylsalicylic acid does not permit a differentiation between the two mechanisms. However, a determination of the products formed in the reac-

tions of sodium nitrite and the two other isomeric methylsalicylic acids leads to the conclusion that this decarboxylation occurs primarily through II. With 3-methylsalicylic acid the 2-nitro-6-methylphenol which is isolated can only result from an attack of the nitrosonium ion on the carbon atom containing the carboxyl group (or carboxylate ion). Furthermore, the product recovered from 4-methylsalicylic acid was the 2-nitro-5-methylphenol expected by route II.

4-Hydroxybenzoic acid also undergoes some decarboxylation when treated with sodium nitrite; 4-nitrophenol was ultimately recovered in about 6% yield.

In most of these nitrosodecarboxylations, the nitrosophenol was not recovered *per se* and the derived nitrophenol was only recovered in small yields (5 to 15% conversions). That the nitroso compound is an intermediate and that it can be isolated in good yield were demonstrated with a reaction analogous to the well known decarboxylation of 3,5-dibromo-4-hydroxybenzoic acid by bromine to furnish 2,4,6-tribromophenol.¹ When a solution of 3,5-dibromo-4-hydroxybenzoic acid was treated with sodium nitrite, carbon dioxide was evolved rapidly; acidification of the solution after the reaction was complete gave a quantitative yield of the known 2,6-dibromo-4-nitrosophenol, which in turn was oxidized to the corresponding nitrophenol for purposes of further characterization. The bromodesulfonation of 3,5-dibromo-4-hydroxybenzenesulfonic acid is another related reaction which has recently been shown² by kinetic studies to involve an intermediate with a para-quinonoid structure.

The partial decarboxylation or desulfonation of certain hydroxybenzoic acids or phenolsulfonic acids, respectively, during nitration has been frequently observed and reported.³ An examination of this literature leads to the conclusion that in many cases the products which are formed can only result from a direct attack of an electrophilic re-

agent such as NO_2^+ or NO^+ on the carbon atom with the carboxyl or sulfonate group.

Methyl salicylate and sodium nitrite in aqueous ethanol react very slowly to yield small quantities of dimethyl 5,5'-azosalicylate, identified by its hydrolysis to the known 5,5'-azosalicylic acid.

EXPERIMENTAL⁴

Salicylic acid. From 27.6 g. (0.2 mole) of salicylic acid, 14.0 g. of sodium nitrite, and 250 ml. of water, allowed to stand at room temperature for 5 hr., then steam distilled, there was recovered 0.53 g. of 2-nitrophenol, m.p. 46°.

A rerun, in which the solvent was 200 ml. of 25% aqueous ethanol (by volume) and the reaction time 6.5 hr., gave 0.8 g. of 2-nitrophenol, m.p. 46–47° (undepressed in admixture with authentic 2-nitrophenol). The evolution of gas from this ethanolic system occurred almost immediately and very rapidly; carbon dioxide was qualitatively determined by passing the gas through a freshly filtered solution of barium hydroxide. The nitrophenol was recovered from the alcoholic steam distillate by making the latter strongly basic with sodium carbonate, evaporating to remove the alcohol, acidifying, and cooling.

3-Methylsalicylic acid. 3-Methylsalicylic acid (30.4 g.; 0.2 mole), 14.0 g. (0.2 mole) of sodium nitrite, and 200 ml. of water were mixed. The system was thoroughly flushed with nitrogen and maintained under a nitrogen blanket. After 4 hr. at room temperature with occasional swirling, the solution was warmed during 45 min. to the boiling point and then steam distilled. The yield of nitroresol was 1.1 g., m.p. 68–70°. By acidifying the aqueous mother liquors and cooling, there was recovered 20.2 g. of starting acid. The conversion to nitroresol amounted to 10.7%. Recrystallization from 70% aqueous ethanol yielded flat yellow needles, m.p. 71–72°; reported,⁵ 70°.

Anal. Calcd. for $\text{C}_7\text{H}_7\text{NO}_3$: N, 9.15. Found: N, 9.27, 9.21.

4-Methylsalicylic acid. The same quantities and procedure were used as in the previous experiment, except that 4-methylsalicylic acid, m.p. 179–180°, was employed. One gram of yellow-brown solid, m.p. 54–55°, was obtained by steam-distilling the unacidified reaction mixture; an additional 0.3 g., m.p. 54°, was obtained, by acidification and further steam distillation. The mother liquors were chilled to 0°, the solid was removed by filtration, dried, and extracted with methylene chloride. Impure starting acid (19.4 g.) remained. Oxidation of the dried methylene chloride extracts with peroxytrifluoroacetic acid⁶ and work-up in the usual manner yielded 0.2 g. of nitroresol, m.p. 54–55°. The total recovery corresponded to a conversion of 13.5%. Recrystallization from aqueous ethanol gave yellow needles, m.p. 55–56°; reported⁷ for 2-nitro-5-methylphenol, 56°.

5-Methylsalicylic acid. From 0.1 mole of 5-methylsalicylic acid there was obtained 0.4 g. of yellow, steam-distillable solid, melting at 32–33°C; reported⁸ for 2-nitro-4-methylphenol, 33–34°. Six grams of starting acid, m.p. 152–153°, was recovered.

4-Hydroxybenzoic acid. A solution consisting of 6.9 g. (0.05 mole) of 4-hydroxybenzoic acid, 3.5 g. of sodium nitrite, and 50 ml. of water was held at 48–52° for 10 min.; carbon dioxide was evolved. The solution was then cooled to

(4) The melting points are uncorrected.

(5) G. P. Gibson, *J. Chem. Soc.*, 42 (1925).

(6) This is the procedure of W. D. Emmons, *J. Am. Chem. Soc.*, 76, 3468, 3470 (1954). A trial experiment with 2-methyl-4-nitrosophenol indicated a quantitative conversion to the nitro compound.

(7) G. P. Gibson, *J. Chem. Soc.*, 1269 (1923).

(8) A. Deninger, *J. prakt. Chem.*, [2], 40, 299 (1889); H. T. Upson, *Am. Chem. J.*, 32, 13 (1904).

(1) For example, see E. Grovenstein, Jr. and U. V. Henderson, Jr., *J. Am. Chem. Soc.*, 78, 569 (1956).

(2) L. G. Cannell, *J. Am. Chem. Soc.*, 79, 2927 (1957). See this reference for a list of earlier references on bromodesulfonation.

(3) Typical examples can be found in the following references: (a) Marchand, *J. prakt. Chem.*, [1], 26, 397 (1842); (b) H. Hubner, *Ann.*, 195, 1 (1879); (c) A. Deninger, *J. prakt. Chem.*, [2], 42, 550 (1890); (d) W. Borsche and A. D. Berkhout, *Ann.*, 330, 98 (1904); (e) I. J. Rinkes, *Rec. trav. chim.*, 45, 848 (1926); (f) F. V. Hemmelmayr, *Monatsh.*, 25, 25 (1904); 26, 185 (1905); (g) E. Diepolder, *Ber.*, 29, 1756 (1896); (h) F. Reverdin, *Bull. soc. chim.*, [4] 3, 591 (1908); (i) J. Biehringer and W. Borsum, *Ber.*, 48, 1314 (1915); (j) H. Salkowski, *Ann.*, 367, 350 (1909); (k) H. E. Armstrong, *J. Chem. Soc.*, 869 (1872); (l) H. E. Armstrong and F. D. Brown, *J. Chem. Soc.*, 857 (1872); (m) R. L. Datta and P. S. Varma, *J. Am. Chem. Soc.*, 41, 2041 (1919); (n) G. Dahmer, *Ann.*, 333, 363 (1904); (o) W. Robertson, *J. Chem. Soc.*, 1482 (1902).

15°, acidified with 4 ml. of concentrated hydrochloric acid, and immediately extracted with three 25-ml. portions of methylene chloride. The combined extracts were dried and then oxidized by the Emmons procedure.⁶ Evaporation of the washed and dried methylene chloride solution left 0.45 g. (6.5%) of solid which melted at 112–113.5° after one recrystallization from water. A mixture with an authentic sample of 4-nitrophenol melted at 113.5–114.5°; admixture with 2,4-dinitrophenol depressed the melting point to 75–80°.

2,4-Dihydroxy- and 3-nitro-4-hydroxybenzoic acids. Carbon dioxide was evolved when these acids were warmed with aqueous sodium nitrite on the steam bath; only tars and some starting acid were recovered.

3-Nitrosalicylic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid, and 3,5-dinitro-4-hydroxybenzoic acid. Essentially no carbon dioxide was evolved when these acids were heated with aqueous sodium nitrite solution; oxides of nitrogen were liberated, and the starting acids were recovered unchanged when the reaction solution was acidified.

3,5-Dibromo-4-hydroxybenzoic acid. Sodium nitrite (0.7 g.) was added to a solution of 2.96 g. of the acid in 25 ml. of ethanol and 15 ml. of water. There was an immediate evolution of carbon dioxide and the solution became yellow-green. After the solution had stood overnight at room temperature, it was heated on the steam bath for 10 min., cooled to 5°, and acidified with 1 ml. of concentrated hydrochloric acid. The tan platelets which separated were filtered and washed with cold water. A second crop was obtained by diluting the mother liquors with water. The total yield of compound, which turned dark about 160°, was 2.29 g. Recrystallization from aqueous methanol gave tan needles, decomposing at 168–169°. Forster and Robertson⁹ reported that 2,6-dibromo-4-nitrosophenol darkened about 160° and detonated between 168 and 175°.

Anal. Calcd. for $C_6H_3NO_2Br_2$: N, 4.99; Br, 56.90. Found: N, 4.82, 4.76; Br, 56.16.

Some of this nitroso compound was oxidized in methylene chloride with peroxytrifluoroacetic acid. The impure product melted at 139–140°; recrystallization from ethanol raised the melting point to 142°; Forster and Robertson⁹ reported 142°; Pope and Wood,¹⁰ 144–145°.

3,5-Dibromosalicylic acid was not decarboxylated by aqueous sodium nitrite.

Methyl salicylate and sodium nitrite. Methyl salicylate

(30.4 g.; 0.2 mole), 14.0 g. of sodium nitrite, 500 ml. of 95% ethanol, and 400 ml. of water were mixed and allowed to stand at room temperature for 2.5 months. The solution became dark-orange in color, and orange needles slowly crystallized. The product was removed by filtration, washed with 50% ethanol, and dried; 1.3 g., m.p. 200–205°. Two recrystallizations from large volumes of 95% ethanol gave flat orange needles and raised the melting point to 227–229°, without decomposition but with preliminary shrinking at 222–226°. The compound is soluble in dilute, aqueous sodium hydroxide and can be reprecipitated by acidification; it is very soluble in cold acetone and can also be recrystallized from glacial acetic acid. Both the analyses and the infrared spectrum indicate a dimethyl azosalicylate.

Anal. Calcd. for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.97; H, 4.16; N, 8.58.

Some of the compound (0.3 g.) was heated on the steam bath for 1 hr. with 50 ml. of 0.1*N* sodium hydroxide. Cooling, followed by acidification with glacial acetic acid, furnished a light yellow powder, which was filtered and washed well with cold water. The product was dissolved in aqueous sodium bicarbonate, filtered, heated to boiling, and reprecipitated by the addition of dilute acetic acid. The water-washed, dried compound did not melt up to 300° although some sublimation started between 290 and 295°. The infrared spectrum and the x-ray powder pattern were essentially identical with the respective patterns from an authentic sample of 5,5'-azosalicylic acid.¹¹

Anal. Calcd. for $C_{14}H_{10}N_2O_6$: C, 55.63; H, 3.34. Found: C, 55.18; H, 3.70.

Reaction of the silver salt of authentic 5,5'-azosalicylic acid with methyl iodide also yielded an ester (Found: N, 8.59) whose ultraviolet absorption spectrum in 95% ethanol was identical with that for the product obtained in the methyl salicylate-sodium nitrite reaction ($\lambda_{max.} = 226, 248, 337, \text{ and } 352 \text{ m}\mu$). The infrared spectra corresponded closely. However, this ester partially melted at 183–184°, resolidified, then melted in the range 205–220°C. The reason for this difference in behavior was not determined.

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(9) M. O. Forster and W. Robertson, *J. Chem. Soc.*, 686 (1901).

(10) F. G. Pope and A. S. Wood, *J. Chem. Soc.*, 1823 (1912).

(11) See British Patent 408,676, April 16, 1934 [*Chem. Abstr.*, 28, 5680^a (1934)] for one method of preparing the sodium salt of this acid.