[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

# Investigations in the Retene Field. VI. Retenediphenic Acid and Some of its Derivatives

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By the oxidation of retenequinone with hydrogen peroxide, Fogelberg[2] obtained a sirupy oxidation product, which he converted into retenediphenic anhydride, in 57% yield, by the action of acetyl chloride and acetic anhydride. Hydrolysis of this anhydride gave the desired acid.

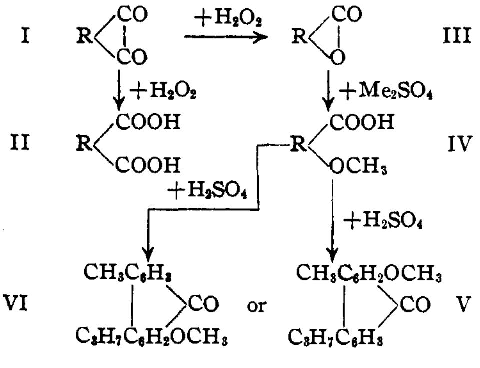
We have now found that retenediphenic acid (II) can be prepared directly in 65% yield, and in crystalline condition, by oxidizing retenequinone (I) in glacial acetic acid solution with 30% hydrogen peroxide.

As a by-product in this reaction, there was formed the lactone (III). This is analogous to the experience of Fieser[3] in the oxidation of 3,6-dimethoxyphenanthraquinone.

The retenediphenic acid, when treated with acetic anhydride, was changed to its anhydride. From the latter, by the action of ammonia and of aniline, an amic and an anilic acid were prepared; and by treatment with methanol and ethanol, the corresponding acid esters. When the anhydride was heated with borneol, or the free acid with glycerol, neutral esters were formed in the nature of pale artificial resins.

FLOW SHEET

In the following formulas, the residue $CH_3\overset{|}{C_6H_3}\overset{|}{C_6H_3}C_3H_7$ is represented by R.



Treatment of retenediphenic acid with sulfuric acid yielded fluorenone derivatives which will be described in another paper.

The lactone (III) was changed to the methoxy acid (IV) by the action of dimethyl sulfate, and this in turn into the fluorenone (V or VI), by treatment with concentrated sulfuric acid.

So far as our experiments have gone, only one of the various possible structural or stereoisomers was formed in these reactions; but which one, has not been proven as yet.

## Experimental

**Retenediphenic Acid.**—To a hot solution of 25 g. of retenequinone, m. p. 197–197.5° (corr.), in 150 cc. of glacial acetic acid, there was added dropwise 55 cc. of 30% hydrogen peroxide at such a rate as to maintain brisk refluxing. Some of the quinone separated during this process, but redissolved when the reaction mixture was boiled. The solution was then refluxed for two hours, at the end of which time the original crimson color had changed to brown. The greater part of the acetic acid was removed by distillation and the cooled residue was poured into 100 cc. of water containing enough dilute sodium hydroxide to neutralize most of the remaining acetic acid. A brown oil formed. The supernatant liquid was decanted and the crude tarry oxidation product was boiled with eight liters of water and filtered. Upon cooling, the filtrate deposited white plates; evaporation of the mother liquor to a small volume yielded more of the desired product. The combined yield was 17.8 g. (65%). Recrystallized from benzene, it appeared as tiny colorless stable crystals, which melted at 191–191.5° (corr.) to a clear liquid without apparent evolution of any vapor. On cooling, this liquid refused to congeal, even when left overnight in an ice box, unless the sides of the tube were scratched with a rod. The colorless re-solidified material melted at 190.5–191° (corr.). Fogelberg[2] reported a melting point of 188–189.5°.

*Anal.* Calcd. for $C_{18}H_{18}O_4$: C, 72.45; H, 6.09. Found: C, 72.32; H, 6.07.

In cold, concentrated sulfuric acid, it dissolved to a crimson solution, the color of which was discharged by dilution.

**Anhydride.**—Prepared from the acid and acetic anhydride, and recrystallized from the latter, it was obtained in stout colorless prisms, m. p. 112–112.5° (corr.); yield, practically that calculated. Fogelberg gave the melting point as 111–112°.

*Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.76. Found: C, 77.16; H, 5.75.

**Acid Methyl Ester.**—Retenediphenic anhydride (1 g.) was boiled with 5 cc. of absolute methanol for fifteen minutes and hot water was added dropwise to the clear solution until incipient cloudiness persisted. Upon cooling and seeding, methyl acid retenediphenate recrystallized

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[1] Fritzsche Fellow in Organic Chemistry, Columbia University, 1935–1936.

[2] Fogelberg, *Ann. Acad. Sci. Fennicae*, Ser. **A29**, No. 4, 3–7 (Komppa-Festschrift) (1927); *Chem. Zentr.*, **98**, II, 2299 (1927).

[3] Fieser, THIS JOURNAL, **51**, 2473 (1929).

in clusters of white needles, m. p. 126–126.5° (corr.); yield, practically quantitative. The compound appeared as an oil from such a methanol–water mixture even when in the pure condition unless seed was used.

*Anal.* Calcd. for $C_{19}H_{20}O_4$: C, 73.04; H, 6.46. Found: C, 73.12; H, 6.65.

Its solution in cold, concentrated sulfuric acid was blood-red; on dilution, the color was lost.

**The acid ethyl ester,** prepared similarly and crystallized from an ethanol–water mixture by seeding, melted at 105–105.5° (corr.).

*Anal.* Calcd. for $C_{20}H_{22}O_4$: C, 73.58; H, 6.80. Found: C, 73.32; H, 6.85.

**Neutral Bornyl Ester.**—A mixture of 2.8 g. of retenediphenic anhydride and 3 g. of borneol was heated at 140° for three hours. The neutral bornyl ester thus obtained possessed a pale amber color and exhibited the properties of an artificial resin.

**Neutral Glyceryl Ester.**—This was prepared in similar fashion by heating retenediphenic acid and glycerine in stoichiometric proportions. The neutral glyceryl ester was similar to the bornyl ester in its properties, but was somewhat lighter in color.

**The amic acid** was prepared by the action of concentrated ammonium hydroxide solution upon the anhydride, which was the method used by Fogelberg, who recorded the melting point as 196–197°. Our product was obtained in practically the calculated yield, crystallized from 95% ethanol in colorless hard prisms, which melted at 201–202° (corr.) to a colorless clear liquid, without evolution of gas. When cooled, the melted compound re-congealed and then remelted at the same point.

*Anal.* Calcd. for $C_{18}H_{19}O_3N$: C, 72.69; H, 6.45. Found: C, 72.58; H, 6.34.

In similar manner, the **anilic acid** was produced, by refluxing a mixture of the anhydride (1 g.) with aniline (5 g.) for twenty minutes, cooling and pouring the mixture upon cracked ice containing some hydrochloric acid. The precipitated crude acid was collected, washed with dilute hydrochloric acid, then with water, and dried at 110°; yield, practically that calculated. From 95% ethanol, it crystallized in clusters of colorless needles, which melted at 251–252° (corr.) to a pale brown liquid, without apparent charring or evolution of vapor. Like the retenediphenic acid, the fused material refused to solidify on standing until the sides of the containing vessel were scratched with a glass rod. It then set to a pale cream-colored solid, which melted at 248–249° (corr.), indicating that some slight decomposition had been caused by the first melting. Both the amic and the anilic acid, when heated for two hours at 250°, yielded dark viscous oils which were not investigated.

*Anal.* Calcd. for $C_{24}H_{23}O_3N$: C, 77.15; H, 6.21. Found: C, 77.21; H, 6.39.

**Methylisopropylhydroxybiphenylcarboxylic Lactone (III).**—The water-insoluble residue (2.5 g.) obtained in the oxidation of the retenequinone, crystallized from 95% ethanol in colorless long silky needles (1 g. or less), m. p. 137–137.5° (corr.), which dissolved very slowly when boiled with 10% aqueous caustic alkali. When this alkaline solution was acidified, the lactone separated and not the hydroxy acid.

*Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 80.97, 80.92; H, 6.32, 6.51.

**Methylisopropylmethoxybiphenylcarboxylic Acid (IV).**—A strongly alkaline solution of the lactone was shaken with an excess of dimethyl sulfate until a precipitate began to settle out, when it was boiled for a short time, cooled, and acidified. The crude compound which separated was dissolved in a sodium carbonate solution, the solution filtered and the product reprecipitated by acidification. Crystallized from dilute ethanol, it formed minute colorless prisms, m. p. 122–122.5° (corr.); yield, practically that calculated.

*Anal.* Calcd. for $C_{18}H_{20}O_3$: C, 76.01; H, 7.10. Found: C, 76.02; H, 6.97.

**Methylisopropylmethoxyfluorenone-9 (V or VI).**—The foregoing acid dissolved in cold concentrated sulfuric acid to a crimson solution which after fifteen minutes was poured into ice water. The yellow crystalline precipitate was removed, washed with dilute caustic alkali, then with water, and was crystallized from 95% ethanol. There resulted long transparent yellow needles, m. p. 126–126.5° (corr.); yield, practically that calculated.

*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 80.71; H, 6.80.

## Summary

1. Retenediphenic acid has been obtained directly, in crystalline form and 65% yield, by the oxidation of retenequinone in glacial acetic acid solution with 30% hydrogen peroxide.

2. As a by-product, there was isolated the lactone of the methylisopropylhydroxybiphenylcarboxylic acid.

3. The retenediphenic acid behaves like other diphenic acids and a number of derivatives were prepared therefrom. It also resembles phthalic acids in forming artificial resins with glycerol or borneol.

4. From the lactone by-product, there have been prepared the corresponding methoxy acid, and methoxyfluorenone.

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