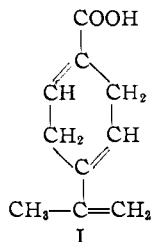


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reactions of Dehydroperillic Acid

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A crystalline acid, m.p. 88°, obtainable from the heartwood of Western Red Cedar was studied by Anderson and Sherrard.² It was named dehydroperillic acid and was assigned structure I.



Some of this compound was prepared for the present study through the courtesy of W. G. Van Beckum of Weyerhaeuser Timber Company.

It was found that the acyl chloride could be prepared by use of thionyl chloride and pyridine but not by thionyl chloride alone, since alkaline hydrolysis of the latter product gave rise to a mixture of carboxylic acids melting over a wide range. Anderson and Sherrard noted that dehydroperillic acid underwent isomerization into cuminic (*p*-isopropylbenzoic) acid when heated with mineral acids. The dehydroperillyl chloride formed in the presence of a little pyridine, however, was readily hydrolyzed to dehydroperillic acid of reasonable purity. Treatment of the acyl halide with ethanol, ammonia or aniline caused conversion to the ethyl ester, amide and anilide, respectively.

The isoprene-like structure of dehydroperillic acid made it seem reasonable to expect ease of polymerization but any such tendency was found to be slight. Attempts to polymerize the ester or the acid by heating with benzoyl peroxide were negative. The butyl-rubber type of polymerization procedure was also unsatisfactory. For these tests we are indebted to P. J. Frolich and W. J. Sparks of Esso Laboratories, Linden, New Jersey. They tested the acid, ester and anilide and found that although resinous products or oils could be obtained both at -23 or -97°, the degree of polymerization was low. Copolymerization experiments with isobutylene were unsuccessful also, since small quantities of dehydroperillic acid or its derivatives inhibited the reaction to such an extent that the only polymers formed were much too low in molecular weight for adequate vulcanizability. If the two double bonds in the ring of structure I were changed so as not

to be conjugated with the double bond of the side chain, the present data would then become more understandable. The unconjugated, terminal methylene group seems necessary, however, to explain formaldehyde on ozonolysis² of I.

Experimental

Crude dehydroperillic acid was purified by crystallization from alcohol. Colorless needles were obtained melting at 85-86.5°.

Dehydroperillyl Chloride.—Five grams of the acid was added gradually into a mixture of 8 g. of thionyl chloride and five drops of pyridine. The temperature dropped rapidly to 10-15° as sulfur dioxide and hydrogen chloride were evolved. The reaction mixture was left at room temperature for twenty minutes after the acid was all added. Gas evolution had ceased at this time. The product was used directly for the preparation of the anilide.

Dehydroperillanilide.—The above crude acyl chloride was added slowly into a mixture of aniline (10 g., an excess) and benzene (60 cc.). A vigorous reaction ensued. The aniline hydrochloride was separated and any excess of aniline in the benzene layer was removed by washing with dilute hydrochloric acid, then with dilute alkali. The crude anilide (6.5 g.) remaining on evaporation of the solvent was crystallized from 75% alcohol; m.p. 97-98°.

Anal. (by T. S. Ma). Calcd. for C₁₆H₁₇NO: N, 5.86. Found: N, 5.68.

Dehydroperillamide.—Five grams of the acid was converted to the acyl chloride as before, and to the latter, dissolved in ether, was added powdered ammonium carbonate until gas was no longer evolved. Water was then added and the ether layer was separated, washed with concentrated ammonium hydroxide, then processed for the amide. Crystallization from 50% alcohol yielded colorless plates of m.p. 95-96°; yield 2 g.

Anal. (by M. Hines). Calcd. for C₁₀H₁₁NO: C, 73.58; H, 8.03. Found: C, 73.43; H, 8.03.

Ethyl Dehydroperillate.—The acid chloride, prepared from 16 g. of acid, was poured slowly into a mixture of 24 g. of absolute alcohol and 14 g. of dry pyridine. After warming the solution for ten minutes on the steam-bath, it was poured into water and the ester was taken up in ether. As finally purified, the ester was collected at 88° (4 mm.); yield, 13 g. or 70%; *d*₂₅²⁵ 0.999. On alkaline hydrolysis, it gave a 95% yield of pure dehydroperillic acid.

Anal. (by T. S. Ma). Calcd. for C₁₂H₁₆O₂: C, 74.96; H, 8.39. Found: C, 73.77; H, 8.26.

Heating with Benzoyl Peroxide.—No polymeric material resulted on heating a mixture of 0.05 g. of benzoyl peroxide and 1.5 g. of dehydroperillic acid at 95° for one day. Similarly, 1.5 g. of the ethyl ester was not changed by heating at 70° with 0.07 g. of the peroxide.

It is of interest to note that when the acid was heated alone at 110° for half an hour, no pyrolysis was evident. The melt crystallized on cooling, m.p. 85-88°.

Summary

Derivatives of dehydroperillic acid are reported. The conjugate unsaturation in the structure of these compounds suggests ready polymerizability which was not experienced in practice.

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(1) Weyerhaeuser Timber Company Fellow, 1943.

(2) Anderson and Sherrard, *THIS JOURNAL*, **55**, 3813 (1933). In a private communication Dr. Anderson advises that Dr. H. Erdtman and associates of the Royal Institute of Technology, Stockholm, are investigating this acid with a view toward more complete elucidation of its structure.