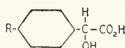


An Oxidation Method for the Proof of the Structure of Substituted Mandelic Acids

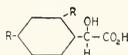
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While preparing various substituted mandelic acids^{1,2} it became necessary to find some method to prove the positions of the substituents on the benzene ring. For the simple cases such as



the problem was solved readily by oxidizing the mandelic acid derivative with excess alkaline potassium permanganate. In the case of the para alkyl-substituted mandelic acids this procedure produced terephthallic acid, the dimethyl ester of which is easily prepared and has a convenient melting point of 140°C.³

But when the problem is more complex in such a case as



it is not desirable to oxidize to the corresponding tricarboxylic acids, especially when small amounts are involved, because these carboxylic acids are relatively hard to purify, their melting points are high, and the melting points of the isomers are in some cases fairly close together. Hence, we sought a method by which it would be possible to oxidize the oxygenated side chain of the mandelic acids to a carboxyl group without effecting the alkyl groups. These alkyl-substituted benzoic acids are in general easy to purify and have satisfactory melting points for identification purposes.

The basis of the method devised to effect the above purpose is the relative ease with which the oxygenated side chain in these compounds is changed to a carboxyl group. It was found that, when a weighed amount of the mandelic acid was dissolved in dilute alkali and just sufficient potassium permanganate was added to oxidize the oxygenated side chain, the alkyl groups were not affected. The method has been applied to eight substituted mandelic acids to prove its general nature.

Although the use of potassium permanganate to oxidize alkyl benzenes is well known, a careful search of the literature failed to reveal an application to this case.

Experimental

Inasmuch as the procedure was the same in each case, only one example will be described in detail. One gram of 2,4-dimethyl mandelic

¹ Riebsomer, Irvine, and Andrews, 1938. Proc. Indiana Acad. Sci., 47, 139.

² Riebsomer, Irvine, and Andrews, 1938. Journ. Amer. Chem. Soc., 60, 1015.

³ Mulliken, 1914. Identification of pure organic compounds. 1, 85. John Wiley, New York.

acid was placed in 125 cc. of water, and 4 cc. of 10% sodium hydroxide was added. This mixture was warmed on a steam bath, and 0.59 g. of potassium permanganate dissolved in 40 cc. of water was added dropwise until the addition of a few drops of the permanganate solution left the solution permanently pink. The reaction proceeded very rapidly. This required practically all the 0.59 g. of permanganate. The excess of permanganate was destroyed with a few drops of sodium bisulphite solution, the manganese dioxide filtered, and the filtrate acidified with hydrochloric acid. A white precipitate formed, which upon crystallization melted at 126-126.5°C., which is the melting point of 2,4-dimethyl benzoic acid.

Table I presents a summary of the data, including the mandelic acids oxidized, the melting points of the oxidation products, and the melting points of the corresponding benzoic acids as reported in the literature.

TABLE I.

Mandelic Acid oxidized	M.p. of Oxidation product °C	Benzoic Acids	M.p. of benzoic acids—reported in literature °C
p-Methyl	176-177	p-Methyl	178-179
p-Ethyl	112-113	p-Ethyl	112-113
p-n-Propyl	141-142	p-n-Propyl	140-141
p-t Butyl	162.5-164	p-t-Butyl	164
p-t-Amyl	158-158.5	p-t-Amyl	158
2,4, Dimethyl	126-126.5	2,4, Dimethyl	126-127
2,5, Dimethyl	131.5-132	2,5, Dimethyl	132
3,4, Dimethyl	163.5-164	3,4, Dimethyl	163

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Summary

An oxidation method to prove the structures of substituted mandelic acids has been presented and eight examples given.