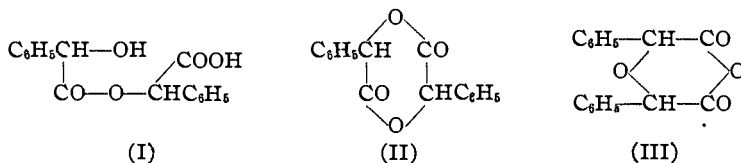


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

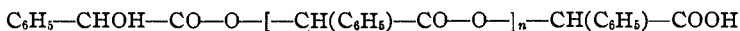
## The Pyrolysis of Mandelic Acid and Related Compounds

BY CHARLES D. HURD AND HARRY R. RATERINK

When  $\alpha$ -hydroxy acids are heated they undergo two different types<sup>1</sup> of dehydration: (1) into esters or inner esters (lactide, etc.), and (2) into a cyclic acid anhydride. For mandelic acid to behave analogously there should be formed mandelylmandelic acid (an ester) (I), the inner ester (II) or dimandelic anhydride (III). The esters (I) and (II) were considered by Bischoff and Walden,<sup>2</sup> who pyrolyzed mandelic acid. Other decomposition products which they reported were benzaldehyde, diphenylmaleic anhydride and a gas thought to be carbon monoxide.



In the present work with mandelic acid it was established that both types of pyrolysis occur. The fact that residues were formed by heating at 200° for two and six hours which possessed average molecular weights of 380 and 500, respectively, and from which mandelic acid could be regenerated on saponification points to polymers of the recurring unit type



(mol. wt. = 420 and 554 when  $n = 1$  and 2). Undoubtedly some cyclic ester (lactide type) was also present. Almost no gases were formed at 200°.

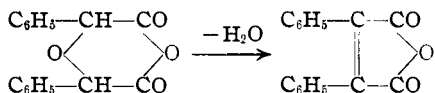
The depression of the melting point of mandelic acid (118° to 106°) noted by Kizhner<sup>3</sup> when he kept it molten (130°) for several hours may be explained on similar grounds. Some mandelylmandelic acid must have been formed and enough of it persisted through the purification process to lower the melting point. To confirm this reasoning, it was found that the equivalent weight of material similarly prepared (mandelic acid heated for nine hours at 150°, then recrystallized from benzene; m. p. 110°) was 157, not 152.

**Anhydride Formation.**—At higher temperatures (250°) diphenylmaleic anhydride and phenylacetic acid are important reaction products. Dimandelic anhydride is the only logical forerunner of these substances, the former being produced from it by detachment of the elements of water

(1) This subject is discussed by Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, New York, 1929, pp. 424-442.

(2) Bischoff and Walden, *Ann.*, **279**, 118 (1894).

(3) Kizhner, *J. Russ. Phys.-Chem. Soc.*, **56**, 15 (1925); *Chem. Abstracts*, **19**, 2940 (1925).



and the latter by detachment of phenylketene which, with water, would give rise to phenylacetic acid:  $\text{C}_6\text{H}_5\text{CH}=\text{C}=\text{O} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ . Benzaldehyde is formed concurrently. The phenylacetic acid was discovered in preliminary work with Mr. Fred E. Smith. As a matter of fact, its molar yield exceeded that of diphenylmaleic anhydride so it is surprising that earlier workers made no mention of it. The phenylacetic acid from mandelic acid *via* dimandelic anhydride and phenylketene is strictly analogous to the formation of diphenylacetic acid from benzilic acid<sup>1</sup> *via* "benzilide" and diphenylketene. "Benzilide" should be renamed dibenzilic anhydride.

**Dimandelic Anhydride.**—In support of this contention, it was found that synthetic dimandelic anhydride pyrolyzed rapidly at 250° into carbon oxides, benzaldehyde, phenylacetic acid, diphenylmaleic anhydride and tar. These were also the products when mandelic acid itself was taken. Less phenylacetic acid was formed as would be expected because of the limited quantity of water available from the anhydride as compared with the acid.

Dimandelic anhydride was synthesized *via* ethyl dimandelate which was prepared as follows:  $\text{PhCHONaCOOEt} + \text{PhCHBrCOOEt} \longrightarrow \text{NaBr} + \text{O}(\text{CHPh---COOEt})_2$ . The ester was hydrolyzed to the acid and the acid converted to dimandelic anhydride by heating with acetic anhydride.

It is conjectural whether the intermediate between mandelic acid and dimandelic anhydride is dimandelic acid  $\text{O}(\text{CHPh---COOH})_2$ , or mandelic anhydride,  $(\text{PhCHOHCO})_2\text{O}$ . Some evidence for the latter was the formation of mandelanilide by interaction of the neutral residue from a 200°-run with aniline, after demonstrating that no action occurred similarly between ethyl mandelate (an ester) and aniline.

It has been assumed that carbon monoxide predominates in the gas from  $\alpha$ -hydroxy acids but from mandelic acid at 250° about equivalent molar amounts of carbon monoxide and carbon dioxide were formed.

**Cyclohexylglycolic Acid,  $\text{C}_6\text{H}_{11}\text{CHOHCOOH}$ .**—Structurally, this acid resembles mandelic (or phenylglycolic) acid. Its course of pyrolysis, however, more resembled lactic (methylglycolic) acid. If the electron attraction of R in  $\text{RCHOHCOOH}$  determines the course of the reaction, this is reasonable, for the order of decreasing electron attraction is phenyl, methyl, cyclohexyl. The chief gas from cyclohexylglycolic acid was carbon monoxide. Hexahydrobenzaldehyde was found but there was no evidence for cyclohexylacetic acid or dicyclohexylmaleic anhydride.

In a preliminary study of **dilactic anhydride**, these reaction products were identified: carbon monoxide, carbon dioxide, acetaldehyde.

### Experimental Part

**Procedure.**—A weighed quantity of substance was placed in a 25-cc. distilling flask which was connected in series to a condenser, a receiver, a three-way stopcock, a drying tube (sulfuric acid), a bulb for carbon dioxide absorption (30% KOH), another drying tube and three-way stopcock, and finally to a gas collecting bottle. The two stopcocks were connected to each other, shunting the absorbing bulbs, to correct for the excess of expanded gas during cooling. In some experiments the carbon monoxide was determined directly by having the air displaced with carbon dioxide prior to a run and by using carbon dioxide as a sweep. The carbon dioxide was removed by alkali.

**Decomposition into Volatile Products.**—The essential data concerning experiments with mandelic acid, dimandelic anhydride and cyclohexylglycolic acid are summarized in Table I. Gas began to appear at 210–220° but the bath temperature could be raised quite rapidly to 250°, where it was maintained until gas evolution ceased. Nothing but water and aldehyde was found in the liquid distillate. In the first run with mandelic acid, for example, there was 2.23 g. of distillate and 6.29 g. of residue. The 2.23 g. was shown to contain at least 1.19 g. of benzaldehyde *via* benzaldehyde phenylhydrazone and the weight of water was taken as the difference or 1.04 g.

TABLE I  
VOLATILE PRODUCTS OF THE REACTION

Subs. taken, g.	Duration of heating, hours	Products formed				Moles of products formed for each 10 moles of substance taken			
		CO <sub>2</sub> , g.	CO, cc.	H <sub>2</sub> O, g.	Aldehyde deriv., <sup>a</sup> g.	CO <sub>2</sub>	CO	H <sub>2</sub> O	Aldehyde <sup>b</sup>
Mandelic Acid									
10	2.5	0.730	344	1.04	2.20	2.51	2.32	8.8	1.70
10	2.5	.870	336	1.32	2.92	3.00	2.27	11.1	2.26
10	2.5	.750	406	..	..	2.57	2.74	..	..
Dimandelic Anhydride									
5.1	2.0	.236	253	0.15	0.9	2.84	5.95	4.4	2.48
Cyclohexylglycolic Acid									
2.17	0.5	.026	...	..	..	0.4	..	..	..
1.96	0.5	.041	...	..	..	0.7	..	..	..
1.09	2.0	.066	...	.27	.38	2.2	..	21	2.7
0.60	2.0	<sup>c</sup>	53.8	..	..	..	6.2	..	..
1.59	2.0	<sup>c</sup>	149	..	..	..	6.7	..	..
1.59	2.5	<sup>c</sup>	116	.27	.39	..	5.2	15	2.2
1.58	2.0	<sup>c</sup>	131	.24	.50	..	5.9	13	2.9

<sup>a</sup> Benzaldehyde phenylhydrazone, m. p. 155°, from mandelic acid or dimandelic anhydride; hexahydrobenzaldehyde semicarbazone, m. p. 172°, from cyclohexylglycolic acid. These were collected in a Gooch crucible and dried at 100° for one hour before weighing. <sup>b</sup> Benzaldehyde or hexahydrobenzaldehyde. <sup>c</sup> Carbon dioxide atmosphere maintained; gas collected over 10% KOH solution.

**The Residue from Mandelic Acid.**—The phenylacetic acid was extracted from the 6.29 g. of residue in the first run with cold 10% sodium hydroxide solution. The solution was acidified, the precipitate collected and crystallized from hot water. The white crystals of phenylacetic acid weighed 1.18 g.; m. p. (and also mixed m. p.), 71–72°.

The more insoluble diphenylmaleic anhydride was extracted by hot 10% sodium hydroxide solution. Acidification gave a red precipitate which was recrystallized from ethyl acetate. The yellow crystals melted at 154–155°; weight, 1.86 g. These weights

correspond to 1.32 and 1.13 moles, respectively, of phenylacetic acid and diphenylmaleic anhydride for each ten moles of mandelic acid taken.

**The Residue from Dimandelic Anhydride.**—By extracting this residue similarly with cold and then hot 10% alkali solution there was isolated 0.38 g. of yellow diphenylmaleic anhydride (m. p. 150–152°) and a small quantity of white phenylacetic acid (m. p. 69–71°). When the diphenylmaleic anhydride was heated with aniline, it changed to diphenylmaleic phenylimide,<sup>4</sup> of m. p. 170–171° after crystallization from alcohol.

**The Residue from Cyclohexylglycolic Acid.**—This was a dark red resin from which nothing was extracted by cold potassium hydroxide solution. Hence, acids were not formed in the pyrolysis. About three-fourths of the residue was soluble in hot 10% potassium hydroxide solution.

**Dilactic Anhydride.**—A 10.8-g. portion of this material was passed through a tube in an electrically heated furnace at 550° during one hour. From the effluent vapors, 1.4 g. of acetaldehyde was condensed in a spiral cooled by ice-salt. Its identity was confirmed by the aniline derivative,<sup>5</sup>  $\text{CH}_3\text{CH}(\text{NHC}_6\text{H}_5)\text{CH}_2\text{CH}=\text{NC}_6\text{H}_5$ , m. p. 126°. The large volume of gas was carbon monoxide and carbon dioxide in about the ratio of 4:1 by volume.

**Mandelic Acid at 150°.**—When 15 g. of mandelic acid was heated for nine hours at 150° and 20 mm., 1 g. of water was collected as distillate. The residue was soluble in ether and completely extracted therefrom by a 10% solution of sodium hydroxide. Acidification of the alkaline extract and crystallization of the precipitate from benzene gave a substance melting at 110°. Its neutral equivalent was 156.7. A mixed melting point value of 112–114° was obtained with known mandelic acid of m. p. 116° and of neutral equivalent 152.2 (experimental).

**Mandelic Acid at 200°.**—Ten-gram samples were used. In the distillates, 1 g. of water and 0.3 g. of benzaldehyde were identified. The resinous residue (R) from a ten-hour heating at 200° (10 mm. or 760 mm.) contained no mandelic acid, for it was insoluble in sodium carbonate solution. Furthermore, it was much more soluble in benzene than mandelic acid. The latter crystallizes readily from hot benzene on cooling, but (R) did not separate. From hot diamyl ether solution, a nondescript material, m. p. 65–75°, separated on cooling.

(R) was freed of traces of mandelic acid by stirring for ten minutes with sodium carbonate solution. To some of the residue, aniline was added in excess and the excess was distilled off at ordinary pressure. Mandelanilide, m. p. 146°, was easily isolated from the non-volatile portion. When ethyl mandelate was treated similarly with aniline, no mandelanilide was isolable.

(R) was soluble in hot 20% sodium hydroxide solution. The 110° crystals were again encountered on acidification and crystallization from benzene.

A 10-g. portion of (R), when pyrolyzed at 250° as described above, gave (in g.):  $\text{C}_6\text{H}_5\text{CHO}$ , 0.9;  $\text{H}_2\text{O}$ , 0.3;  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ , 0.8; diphenylmaleic anhydride, 1.7;  $\text{CO}_2$ , 0.86; and 3.64 cc. of  $\text{CO}$ .

(R) from a two-hour run gave molecular weight values of 370, 390, 360, 390, 397 (average, 381) by the ebullioscopic method in acetone. (R) from a six and one-half hour run gave values of 529, 492, 492 (average, 504). The calculated molecular weight of mandelic acid is 152.

**Synthesis of Reagents.**—Mandelic acid was synthesized by the method in "Organic Syntheses" (Vol. VI, p. 58). Cyclohexylglycolic acid was made by the method of Godchot and Frezouls.<sup>6</sup> The melting point of 130° given by these authors was confirmed but it differs from the value (166°) of Zelinsky and Schwedoff.<sup>7</sup> Hexahydrobenzaldehyde,

(4) Anschütz and Bendix, *Ann.*, **259**, 65 (1890), found the m. p. to be 174–175°.

(5) Eckstein, *Ber.*, **25**, 2030 (1892); Miller, *ibid.*, **25**, 2072 (1892).

(6) Godchot and Frezouls, *Compt. rend.*, **150**, 1248 (1910).

(7) Zelinsky and Schwedoff, *Ber.*, **41**, 2676 (1908).

which was required for this synthesis, was made in better yields *via* cyclohexylmagnesium chloride and ethyl orthoformate (followed by hydrolysis) than by dehydrogenation of cyclohexylcarbinol.

**Ethyl Dimandelate**,  $O(CHPh-COOC_2H_5)_2$ .—The sodium salt of ethyl mandelate was prepared from 7.4 g. of finely cut sodium and 65 g. of ethyl mandelate in 200 cc. of dry ether. Stirring was maintained for seven hours. Then 78 g. of ethyl phenylbromoacetate was added. Considerable heat was evolved. The reaction mixture was left overnight. To work up the products these steps were taken: addition of a carbon dioxide stream; then water to dissolve the sodium bromide; separation, drying and distillation of the ether layer. The unused reactants were taken off up to  $170^\circ$  (22 mm.) and the crude ethyl dimandelate from  $170$ – $218^\circ$  (8 mm.). Redistillation of the latter gave the pure ester, b. p.  $215$ – $216^\circ$  at 8 mm. It was viscid but it would not crystallize; yield, 32 g., or 30% of the theoretical.

*Anal.* Subs., 0.1754, 0.2158:  $CO_2$ , 0.4608, 0.5604;  $H_2O$ , 0.1041, 0.1268. Calcd. for  $C_{20}H_{22}O_4$ : C, 70.1; H, 6.47. Found: C, 71.6, 70.8; H, 6.59, 6.53.

**Dimandelic Acid Hydrate**,  $O(CHPhCOOH)_2 \cdot H_2O$ .—Ethyl dimandelate was refluxed for five hours with 25 g. of potassium hydroxide and 100 cc. of water. Acidification of the cooled solution threw down a thick, red oil. After washing, it solidified and gave beautiful white crystals after two crystallizations from water. The acid was soluble in ether, alcohol, acetone, ethyl acetate and sparingly soluble in hot benzene; but water was the best crystallizing medium. The yield was 15 g. or 53%.

*Anal.* Subs., 0.1578:  $CO_2$ , 0.3662;  $H_2O$ , 0.0761. Calcd. for  $C_{18}H_{14}O_6$ : C, 67.2; H, 4.90. Calcd. for  $C_{18}H_{16}O_6$ : C, 63.2; H, 5.31. Found: C, 63.3; H, 5.35. *Neutral Equiv.* Subs., 0.4219: cc. of 0.08806 *N* alkali, 31.33. Calcd. for  $C_{18}H_{16}O_6$ : equivalent weight, 152.1. Found: 152.9.

The acid did not melt sharply but softened slowly over a wide range,  $120$ – $130^\circ$ . Apparently dehydration was occurring. Its practical insolubility in cold water delineated it sharply from mandelic acid.

**Dimandelic Anhydride**.—Five grams of dimandelic acid hydrate was refluxed for a short time with acetic anhydride, some of the solvent removed and the residue cooled. White, needle-like crystals (2.6 g.) of dimandelic anhydride separated and more was obtained later from the filtrate. After drying over potassium hydroxide in a desiccator the solid melted at  $152$ – $154^\circ$ .

*Anal.* Subs., 0.1810:  $CO_2$ , 0.4725;  $H_2O$ , 0.0750. Calcd. for  $C_{16}H_{12}O_4$ : C, 71.6; H, 4.48. Found: C, 71.2; H, 4.64.

**Dilactic Anhydride**.—Jungfleisch and Godchot's directions<sup>8</sup> for the synthesis of ethyl dilactate were satisfactory:  $NaOCHMeCOOEt + BrCHMeCOOEt \rightarrow O(CHMeCOOEt)_2 + NaBr$ . Their directions for hydrolysis to dilactic acid and thence to the anhydride were inadequate. The trouble was caused by (1) the presence of unhydrolyzed ester, (2) the incomplete anhydridization by vacuum distillation alone. These directions were adopted after considerable search in preliminary experiments.

Ethyl dilactate (48 g.) was refluxed for nine hours with 100 cc. of alcohol and 20 g. of sodium hydroxide, 25 cc. of water being added at the end of three hours. Then the alcohol was distilled off and water added. Any unhydrolyzed ester was removed at this point by ether extraction. Then the aqueous layer was acidified (sulfuric acid), ether extracted and the ether removed. This dilactic acid was refluxed for one-half hour with acetic anhydride. On fractionation, the portion boiling at  $125$ – $128^\circ$  (33 mm.) was collected. It remained liquid. The yield of pure anhydride, based on the total ester taken, was 74%.

(8) Jungfleisch and Godchot, *Compt. rend.*, **144**, 979 (1907); **145**, 7 (1907).

*Anal.* Subs., 0.3356, 0.2838; cc. of 0.1062 *N* alkali, 43.69, 36.73. Calcd. for  $C_8H_8O_4$ : equivalent weight, 72. Found: 72.3, 72.7.

The necessity for the removal of the ester was shown by the high neutral equivalent value of 85 which was obtained when the step was omitted.

### Summary

Mandelic acid undergoes an esterification process at  $200^\circ$  or below into  $\text{PhCHOHCO—O—(CHPhCOO)}_n\text{—CHPhCOOH}$  but the pyrolysis into diphenylmaleic anhydride and phenylacetic acid at  $250^\circ$  is best explained by assuming the transitional, concurrent existence of dimandelic anhydride. This is similar to the known transformation of benzilic acid into dibenzilic anhydride (benzilide). The other products from mandelic acid at  $250^\circ$  are water, benzaldehyde, carbon dioxide and carbon monoxide.

Ethyl dimandelate, dimandelic acid hydrate and dimandelic anhydride were synthesized. Dimandelic anhydride pyrolyzed at  $250^\circ$  in the manner of mandelic acid. A preliminary study was made of dilactic anhydride.

Cyclohexylglycolic acid decomposed at  $250^\circ$  into carbon monoxide and hexahydrobenzaldehyde, presumably through intermediate esters of the type mentioned with mandelic acid. In contrast to mandelic acid, the yield of carbon dioxide was small and there was no evidence for the formation of acid anhydrides as intermediate products.

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## Certain Dichloronaphthalenes and Related Intermediates

BY R. W. BEATTIE<sup>1</sup> AND FRANK C. WHITMORE

Although all of the ten dichloronaphthalenes have long been known, the literature contains a remarkably small amount of information regarding their preparation and properties. The present research was undertaken to produce 50–100 g. samples of 1,2-, 1,4-, 1,5- and 2,6-dichloronaphthalenes in a high state of purity.

The methods recorded in the literature for making the intermediates and the dichloro compounds are given in too little detail to be of any great help in this work. In each case various suggestions obtained from the literature were tested and modified until combinations of real preparative value were developed. The processes evolved represent an unusual amount of laborious experimentation and consequently are recorded in some detail.

(1) Submitted in partial fulfillment of the requirements for the Ph.D. degree at the Pennsylvania State College.