

abruptly upward and increase the intercepts by about one conductance unit.

No recent direct determination of  $\Lambda_0$  at 25° for zinc sulfate has come to our attention, but Courrell, Hamilton and Butler<sup>27</sup> published data which, according to their observed slopes, would lead to  $\Lambda_0 \simeq 125.9$  for zinc chloride or  $\lambda_0 \simeq 49.6$  for the zinc ion. Using  $\lambda_0 = 79.6$  for the sulfate ion, derived from Shedlovsky's value of  $\Lambda_0$  for sodium sulfate quoted by Longworth,<sup>28</sup> our values of  $\lambda_0$  for the zinc and copper ions would be 53.1 and 53.9, respectively.

### Summary

The specific conductivities and *p*H values of

(27) Courrell, Hamilton and Butler, *Proc. Roy. Soc. (London)*, **A147**, 418 (1934).

(28) Longworth, *This Journal*, **57**, 1185 (1935).

dilute zinc and copper sulfate solutions were measured at 25°. The results were corrected for hydrolysis, and the equivalent conductances of the hypothetical unhydrolyzed salts reported at even values of  $\sqrt{C}$ .

The limiting equivalent conductances and "ionization constants" of the salts were estimated by several procedures based upon the interionic attraction theory and the law of mass action. The dependence of the results upon the nature of the extrapolation function was discussed, and  $\Lambda_0 = 132.8$ ,  $K = 0.0049$  for zinc sulfate, and  $\Lambda_0 = 133.6$ ,  $K = 0.0043$  for copper sulfate were proposed as the most reliable values.

NEW HAVEN, CONN.

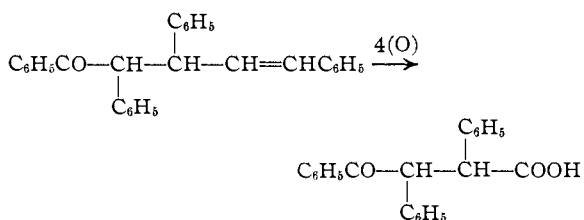
RECEIVED OCTOBER 8, 1938

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE, AND THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## $\alpha,\beta$ -Diphenyl- $\beta$ -benzoylpropionic Acid

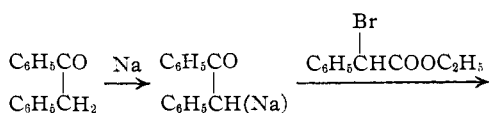
BY H. MARJORIE CRAWFORD

$\alpha,\beta$ -Diphenyl- $\beta$ -benzoylpropionic acid has been prepared by Reimer and Reynolds<sup>1</sup> by the oxidation of  $\alpha,\beta$ -diphenyl- $\gamma$ -benzalbutyrophenone



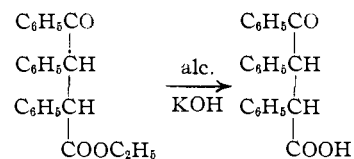
They reported that the acid melted at 211–212° and crystallized from alcohol with one molecule of alcohol of crystallization. They also prepared the methyl ester which melted at 159°.

A simpler method of preparation was sought to obtain considerable quantities of the acid for use in connection with some other work. The following procedure\* was adopted

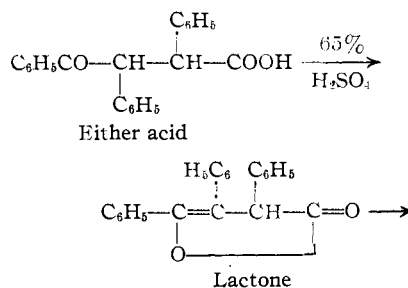


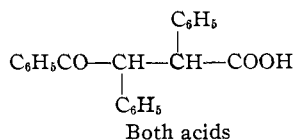
(1) Reimer and Reynolds, *Am. Chem. J.*, **40**, 435 (1908).

\* This method of preparation of the acid and other preparations and analytical results marked with an asterisk formed part of the thesis submitted by Brunhilde Reich as partial fulfillment of the requirements for the degree of Master of Arts at Vassar College.



Analyses and neutralization equivalent ensured the identity of the product, but it consisted of a mixture of the two racemic modifications of the acid, one melting at 201–202° and the other melting at 211–212°. The high melting isomer yields the 159° methyl ester reported by Reimer and Reynolds. The low melting form was formed in much larger quantities. Treatment of either acid with 65% sulfuric acid gave a lactone which must have the double bond in the  $\beta,\gamma$ -position since it can be hydrolyzed to give a mixture of both acids





Rearrangement to the conjugated  $\alpha,\beta$ -unsaturated lactone apparently does not occur in this case, for, if it did, hydrolysis should lead to one new racemic unsaturated hydroxy acid.

### Experimental

**Desoxybenzoin** was prepared in 80% yields from benzoin, using the method of Ballard and Dehn.<sup>2</sup>

**Ethyl  $\alpha$ -bromophenylacetate** was prepared in 85% yields from 136 g. (1 mole) of phenylacetic acid, 240 g. of bromine, 8 g. of red phosphorus and 100 cc. of absolute alcohol. The yield was reduced to 72% when double quantities were used.

**$\alpha,\beta$ -Diphenyl- $\beta$ -benzoylpropionic Acid.**—After trying several methods of making the sodium derivative of desoxybenzoin, the following procedure\* was adopted and gave the acid mixture in about 40% yields. Sodium powder, 2.3 g. (0.1 mole), in dry ether was treated with 19.6 g. (0.1 mole) of desoxybenzoin in a 200-cc. flask fitted with a condenser and guard tube. The mixture was warmed on the steam-bath until the sodium had practically all disappeared. This usually required about an hour and the solution became clear orange in color. Ethyl  $\alpha$ -bromophenylacetate, 20 g. (just under 0.1 mole), was added slowly through the condenser and the heating continued for one and one-half hours. Most of the ether was then evaporated and replaced by alcohol. The mixture was then heated on the steam-bath for two hours with 85 cc. of 15% potassium hydroxide, diluted with water and filtered from unchanged desoxybenzoin and didesyl. Acidifying the filtrate with hydrochloric acid precipitated the keto acids. Several runs were made on double quantities without changing the yield. The acids from several runs were combined for recrystallization.

The low melting acid was formed in much larger quantities, and separated first from the ethyl alcohol solution of the two. Later both forms separated at the same time, but, when crystallization was carried out slowly, they were so different in appearance that the two kinds of crystals could be separated by hand. Further recrystallization of the two acids from alcohol gave pure compounds melting at 201–202° and 211–212°. The low melting acid differed from the high melting one in crystallizing from alcohol without alcohol of crystallization. Both acids are very soluble in chloroform, and acetone, soluble in alcohol, ethyl acetate, ether and benzene, and insoluble in ligroin and water. Ethyl alcohol or acetone and water were the best solvents for recrystallization. The 201° compound formed clusters of stout needles and the 211° compound separated in a mass of very fine needles.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{18}\text{O}_3$  (330): C, 79.98; H, 5.49. Found: C, 79.76; H, 5.67; neut. eq., 324.\*

(2) Ballard and Dehn, *THIS JOURNAL*, **54**, 3970 (1932).

Attempts\* to prepare the oxime and phenylhydrazone of the keto acids were unsuccessful.

**Esters of  $\alpha,\beta$ -Diphenyl- $\beta$ -benzoylpropionic Acid.**—Both ethyl esters could be separated from the original reaction mixture, but it was more satisfactory to prepare the esters from the pure acids by esterifying with the appropriate alcohol and a small quantity of concd. sulfuric acid. The corresponding esters of the two acids did not differ much in solubility. Both methyl esters were very soluble in acetone and chloroform, soluble in benzene and methyl alcohol and only very slightly soluble in ether, ethyl acetate and ligroin. The ethyl esters were very soluble in chloroform, benzene, acetone and ethyl acetate, soluble in ether and ethyl alcohol and insoluble in ligroin.

The methyl ester of the 211° acid melted at 158.5–159° as described by Reimer and Reynolds,<sup>1</sup> and was recrystallized from a mixture of methyl alcohol and acetone.

The methyl ester of the 201° acid was recrystallized from methyl alcohol and melted at 147–148°.

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{20}\text{O}_3$ : C, 80.21; H, 5.85. Found: C, 80.33; H, 6.0.

The ethyl ester of the 211° acid was recrystallized from ethyl alcohol and melted at 138–139°.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{22}\text{O}_3$ : C, 80.40; H, 6.19. Found: C, 80.35; H, 6.32.

The ethyl ester of the 201° acid was recrystallized from ethyl alcohol and melted at 147.5–148°.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{22}\text{O}_3$  (358.7): C, 80.40; H, 6.19. Found: C, 80.44; H, 6.20; mol. wt.,\* 352, 349.

**Lactone.**—When either of the acids was stirred and heated on the steam-bath with 65% sulfuric acid for several hours, the lactone, m. p. 124–125°, resulted.\* It was very soluble in chloroform and ethyl acetate, soluble in alcohol, ether and benzene and insoluble in ligroin.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{16}\text{O}_2$  (312.7): C, 84.59; H, 5.16. Found: C, 84.68; H, 5.26; mol. wt.,\* 318, 313.

Two grams of the lactone was heated under reflux for one hour with 25 cc. of alcohol and 2 g. of potassium hydroxide. The solution was then cooled, diluted with water and acidified with hydrochloric acid. The resulting acid mixture was recrystallized from ethyl alcohol and both acids were recovered, the 201° compound in much larger quantities.

The author wishes to thank the University of Minnesota for the courtesy shown her as an Honorary Fellow of the University while on leave from Vassar College in the spring of 1938.

### Summary

1. A new method of preparing  $\alpha,\beta$ -diphenyl- $\beta$ -benzoylpropionic acid is reported.
2. The two racemic forms of the acid and their methyl and ethyl esters are described.
3. The dehydration of either acid leads to the formation of a lactone.

POUGHKEEPSIE, NEW YORK RECEIVED OCTOBER 31, 1938