

tetracarboxylate dissolved in 40–50 cc. of absolute ether was dropped in through the funnel in thirty to forty minutes. The mixture was refluxed and stirred for an hour. The reaction flask was then cooled with ice water and 25 cc. of 25% ammonium chloride solution was added gradually. Stirring was continued for thirty minutes after all the ammonium chloride solution had been added. The ethereal layer was separated and the aqueous layer containing much solid matter was dissolved in a proper amount of 10% acetic acid and extracted several times with ether. The combined ethereal extracts were evaporated and the residue was then steam-distilled in order to remove most of the biphenyl formed during the reaction. The amount of biphenyl formed (m. p. 67–69°) varied from 0.6–1.2 g. The oil remaining in the distilling flask was extracted with ether and dried over sodium sulfate. The ether was removed and the residual oil was fractionated under reduced pressure. The fraction boiling at 208–210° (5 mm.) was collected. The yield was 4.2 g. (71%).

Anal. Calcd. for $C_{28}H_{20}O_8$: C, 60.9; H, 6.5. Found: C, 61.1; H, 6.2.

Saponification of Ethyl α -Phenylethane- $\alpha,\alpha,\beta,\beta$ -tetracarboxylate.—Forty cc. of 25% potassium hydroxide was refluxed with 1.7 g. of ethyl phenylethane- $\alpha,\alpha,\beta,\beta$ -tetracarboxylate in an oil-bath until the oil had disappeared completely (twelve hours). The aqueous solution was once extracted with ether in order to remove all traces of biphenyl remaining in the ester, then cooled in ice water and acidified with 20% sulfuric acid. An amorphous solid separated. It was filtered and dried on a steam-bath and then pulverized. The white powder was heated in dilute sulfuric acid until complete solution occurred. The solution was combined with the former filtrate and extracted several times with ether. After drying and removing the ether a crystalline substance (0.96 g.) was obtained. The crude acid was crystallized from hot water using a little charcoal. A yield of 0.82 g. of crystals was obtained. It decomposed at about 160°.

Phenylsuccinic Acid.—The acid obtained above was placed in a small glass tube and heated in a sulfuric acid bath keeping the temperature at 170–175° while the carbon dioxide evolved briskly. When the evolution of gas had ceased, 0.77 g. (86% based on the tetra-ester) of crude phenylsuccinic acid was obtained. After one crystallization from water, the pure acid was obtained as fine needles weighing 0.73 g., m. p. 168° (Thorpe reported 168°; Lapworth reported 167°).⁸

Anal. Calcd. for $C_{10}H_{10}O_4$: neut. equiv., 97. Found: neut. equiv., 96.

Ethyl α -Methylethane- $\alpha,\alpha,\beta,\beta$ -tetracarboxylate.—The procedure was similar to that used for the preparation of ethyl phenyl-ethanetetracarboxylate. From 4.7 g. of ethyl ethylenetetracarboxylate 3.8 g. (79%) of ethyl methyl ethanetetracarboxylate was obtained as a slightly yellowish oil boiling at 165–166° (5 mm.).

Anal. Calcd. for $C_{16}H_{24}O_8$: C, 54.2; H, 7.2. Found: C, 54.4; H, 7.8.

Methylsuccinic Acid.—In a 150-cc. 2-necked round-bottomed flask, which was fitted with a reflux condenser and a mechanical stirrer, 2.4 g. of ethyl methylethane-tetracarboxylate and 40 cc. of 20% potassium hydroxide were heated under reflux with stirring for seven hours. The solution was acidified and then extracted with ether.

The aqueous layer was further extracted with ether in a continuous extraction apparatus. The ethereal extracts were combined and dried. After the solvent had been removed, an oil was obtained which was then heated at a temperature 150–160° until no more carbon dioxide was evolved. The residue was dissolved in water, decolorized, and evaporated to dryness. The residual oil solidified slowly in the desiccator. It was crystallized from a mixture of petroleum ether and chloroform. The pure acid was obtained as beautiful crystals, m. p. 110–111° (Boettinger reported 112.5°; Bone and Sprankling reported 110°).⁹ The melting point was not depressed by mixing with an authentic specimen.

Ethyl α -Ethylethane- $\alpha,\alpha,\beta,\beta$ -tetracarboxylate.—The procedure was similar to that used in the previous experiment. The Grignard reagent was prepared from 6.5 g. of ethyl bromide and 1.4 g. of magnesium shavings and allowed to react with 4.2 g. of ethyl ethylenetetracarboxylate. The crude product was obtained as a yellowish oil. The oil was allowed to stand for a few days. The crystals which separated were filtered and washed with a small amount of cold alcohol. On further standing a second crop of crystals was obtained. The process was repeated until no more crystals separated. The total amount of crystals weighed about 1.8 g., m. p. 76°. The melting point was not depressed by mixing with ethyl ethane- $\alpha,\alpha,\beta,\beta$ -tetracarboxylate. The oil, freed from the reduced compound, was fractionated under reduced pressure. The fraction boiling at 180–183° (6 mm.) was collected. The product was of pale yellow color and weighed 2.6 g. (56%).

Anal. Calcd. for $C_{18}H_{26}O_8$: C, 55.5; H, 7.5. Found: C, 54.8; H, 7.0.

Ethylsuccinic Acid.—The saponification of the ester was similar to that of the ethyl methylethanetetracarboxylate. The decarboxylation was carried out at a temperature of 150–160° for thirty minutes. The product was decolorized in hot water. On evaporation, 0.37 g. (36% of the theoretical amount based on the tetra-ester) of oil remained. The oil solidified completely on standing. It was crystallized from chloroform–petroleum ether mixture, and the pure ethyl succinic acid melting at 98–98° (Huggenberg reported 98°; Polk reported 97°)¹⁰ was obtained as fine crystals.

Anal. Calcd. for $C_8H_{10}O_4$: neut. equiv., 73. Found: neut. equiv., 73.

Summary

1. The mode of addition of both aryl and alkylmagnesium bromide to ethyl ethylenetetracarboxylate has been shown to take place exclusively 1:4.

2. A general method for the preparation of monosubstituted succinic acids has been described and phenyl-, methyl- and ethyl-succinic acids were synthesized in this way.

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(9) Boettinger, *Ber.*, **11**, 1352 (1878); Bone and Sprankling, *J. Chem. Soc.*, **75**, 860 (1899).

(10) Huggenberg, *Ann.*, **192**, 149 (1879); Polk, *ibid.*, **242**, 122 (1887).