then the ether was partially driven off, replaced with benzene and the mixture again refluxed for two hours. The mixture was poured into water, the water layer separated and cooled with ice. Cold dilute hydrochloric acid was added slowly with stirring. A yellow, crystalline precipitate formed in a few minutes. This was filtered, washed several times with a little ether and dried in vacuum. The yield was poor and only about a gram of the new toluid was obtained.

0.2 g. subst. gave 10.0 cc. N_2 at 20° and 756 mm.
Calc. for $C_{16}H_{13}NS$: N, 5.6. Found: N, 5.8.

Properties of Phenylpropiolthio-*m*-toluid.—It is soluble in alcohol, ether, benzene, etc. It crystallizes from alcohol in fine, slender, yellow needles. It is best purified by digestion with small portions of warm ether in which it is only slightly soluble. It melts with decomposition at 118–120°. It is readily soluble in sodium hydroxide solution from which it is precipitated by the addition of an excess of acid. No polymerized form was observed. When heated with aqueous or alcoholic sodium hydroxide it changes into a tar. The amount of thiotoluid was insufficient to permit an investigation of the action of phenylhydrazine and hydroxylamine, although small test tube experiments indicated that a reaction takes place in each case with the elimination of hydrogen sulfide.

The Action of *o*-Tolyl Mustard Oil on Sodiumphenylacetylene.—Two grams of phenylacetylene were converted into the sodium derivative, in ether, and the molecular equivalent of *o*-tolyl mustard oil added. No apparent change took place, so the mixture was refluxed for eight hours. It was then poured into water and the two layers separated. The water extract was cooled with ice and acidified in the usual manner. A small amount of a dark-colored oil separated out. It did not solidify on standing and was not further examined. The ether extract in addition to considerable unchanged mustard oil and phenylacetylene contained a small amount of a substance which separated on the sides of the beaker in shining nearly colorless plates. This crystalline mass proved to be a sodium derivative, soluble in water, which on the addition of acid reprecipitated as an oil.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE IDENTIFICATION OF ACIDS. II.

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In a recent article[1] it was shown that the *p*-nitrobenzyl esters of many acids are readily prepared and have properties which render

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them useful for the identification of acids. This study has been continued and derivatives of a number of other acids have been prepared. Essentially the same method of work has been adhered to except that *p*-nitrobenzyl chloride and iodide have been used in some cases in place of the bromide, which was used exclusively in the earlier work. All three of these halides give the same results, though the high molecular weight and slight solubility of the iodide are sometimes disadvantageous.

An effort has been made to prepare mono- as well as di-esters of several dibasic acids. This has usually resulted in failure as, in all except one case, the mono-sodium salt of the dibasic acid has yielded the di-*p*-nitrobenzyl ester. In case of malic acid both mono- and di-esters have been obtained.

Materials and Method of Work.

The *p*-nitrobenzyl bromide was prepared as before, the *p*-nitrobenzyl chloride was obtained by nitrating benzyl chloride, and the iodide was made by boiling either of these with an excess of potassium iodide in dilute alcohol.

The sodium salts of the acids were prepared by dissolving 1 g. of the acid in 25 cc. of water and neutralizing with caustic soda solution, with phenolphthalein paper as indicator, the solution being left distinctly acid. The solution of the sodium salt was evaporated on steam bath, to crystallization or to dryness.

Recrystallization of the esters was carried on, as before, till constant melting points were obtained. The designation of various crops of crystals is the same, *e. g.*, "2nd 1st" means second crystallization, first crop. The materials were weighed on small hand scales and variations of several hundredths of a gram are to be expected.

The experimental work is given in detail, so that the results may be used by those wishing to separate or identify any of these acids.

The melting points were all taken by a different observer but with the same thermometer that was used in the previous work.

RESULTS.

Esters of Monobasic Acids.

Thiocyanic Acid.—This ester was included in former work, but its preparation was repeated using different materials. A mixture of 0.55 g. ammonium thiocyanate and 1 g. *p*-nitrobenzyl chloride with 15 cc. 63% alcohol was boiled one hour. Cooling produced an emulsion which soon crystallized. The 1st 1st was 1.15 g., m. 83.3° and 1st 2nd, 0.07 g., m. 85.5°. The 1st 1st was recrystallized from 10 cc. 63% alcohol and gave 2nd 1st 1.05 g., m. 84.1° and 2nd 2nd, 0.01 g., m. 84°. The 2nd 1st was dissolved in 15 cc. 63% alcohol and gave 3rd 1st 0.77 g., m. 85° and 3rd 2nd 0.07 g., m. 84.5°. Two more crystallizations from the same amount of alcohol gave 4th 1st 0.75 g., m. 85.5°, 4th 2nd 0.08 g., m. 85°, 5th 1st 0.50 g., m. 85°, and 5th 2nd 0.08 g., m. 85°.

The result agrees exactly with the previous work.

Phenylacetic Acid.—A mixture of 1 g. of the sodium salt, 1 g. *p*-nitrobenzyl bromide and 15 cc. 63% alcohol was heated one hour and during this time 10 cc. of the same alcohol was added to keep the ester in solution.

The ester separated as an emulsion which soon became crystalline. The 1st 1st was 1.25 g., m. 63.8° and 1st 2nd 0.02 g., m. 63°, calculated 1.25 g. The 1st 1st was dissolved in 25 cc. 63% alcohol and gave 2nd 1st, 1.18 g., m. 65°, and 2nd 2nd 0.03 g., m. 65°. Recryallization gave 3rd 1st 1.15 g., m. 65° and 3rd 2nd 0.02 g., m. 65°.

Cinnamic Acid.—A mixture of 1 g. of the sodium salt, 1 g. of the bromide and 15 cc. 63% alcohol was boiled one hour. As the ester separated from the hot solution, 30 cc. of the same alcohol was added to keep it in solution. The 1st 1st was 1.15 g., m. 116.8°, 1st 2nd only a trace, calculated, 1.31 g. Recrystallization from 75 cc. 63% alcohol gave 2nd 1st 1.15 g., m. 116.7°, 2nd 2nd negligible.

Hydrocinnamic Acid.—One gram of the sodium salt, boiled with 1 g. of the bromide and 15 cc. 63% alcohol for one hour, gave, on cooling, an oil which crystallized only after several days. The 1st 1st was 0.93 g., m. 32°, 1st 2nd, an oil, calc. yield 1.32 g. The 1st 1st was recrystallized from 20 cc. 63% alcohol, seeding with a bit of the solid ester, giving 2nd 1st 0.88 g., m. 35.5° and 2nd 2nd only a trace. Recrystallization from same amount of alcohol gave 3rd 1st 0.64 g., m. 36.4°, 3rd 2nd, inappreciable. The next was from 15 cc. of the same alcohol and was 4th 1st 0.64 g., m. 36.4°.

Another preparation was made from a sample of the sodium salt from another source. This melted at 34° without recrystallization and gave, with the above, a mixed melting point of 36.2°.

Hippuric Acid.—A mixture of 1 g. of the sodium salt, 1 g. of the bromide, and 15 cc. 63% alcohol boiled one hour gave a beautiful crystalline precipitate. The 1st 1st was 1.18 g., m. 136° and 1st 2nd 0.02 g., m. 80°, calculated 1.45 g. Recrystallization from 15 cc. 63% alcohol gave 2nd 1st 1.10 g., m. 136° and 2nd 2nd 0.02 g., m. 135°. This is a beautiful compound.

***m*-Toluic Acid.**—The mixture consisted of 0.9 g. of the sodium salt, 1 g. *p*-nitrobenzyl chloride and 15 cc. 63% alcohol. As the ester began separating during the hour's boiling, 15 cc. of the same alcohol was added. The 1st 1st was 0.93 g., record of melting point lost, and 1st 2nd 0.23 g., m. 67.5°, mostly unchanged reagent, calculated yield, 1.59 g. The 1st 1st was recrystallized from 33 cc. 63% alcohol and gave 2nd 1st 0.75 g.,

m. 84° and 2nd 2nd 0.16 g., m. 69° (reagent). Recrystallization from 23 cc. 63% alcohol yielded 3rd 1st 0.62 g., m. 86.5° and 3rd 2nd 0.05 g., m. 65° (reagent). Further recrystallization from 20 cc. 63% alcohol gave 4th 1st 0.55 g., m. 86.6°. It appears from this experiment that the chloride did not react completely even in one hour's boiling.

Salicylic Acid.—A mixture of 1 g. sodium salicylate, 1 g. bromide and 15 cc. 63% alcohol was boiled one hour. As the ester separated during this time, 20 cc. more of the alcohol was added. It crystallized at once. The 1st 1st was 0.93 g., m. 96.5° and 1st 2nd 0.05 g., m. 70.5°. Recrystallization from 35 cc. 63% alcohol gave 2nd 1st 0.86 g., m. 96.3°, 2nd 2nd, inappreciable. As the melting point 96.3° is rather near that of the reagent, 99°, a mixed melting point was made of the two and was 93°, showing that they are not the same. The ester is much less soluble than the bromide.

***m*-Hydroxybenzoic Acid.**—A mixture of 1 g. of the sodium salt, 1 g. of the bromide and 15 cc. 63% alcohol was boiled one hour. There was no separation of ester. The hot solution was decanted from a small amount of sediment. On cooling an emulsion was formed which became crystalline after some hours. The 1st 1st was 0.55 g., m. 106°, 1st 2nd 0.60 g., m. 106°. Recrystallization from 17 cc. 63% alcohol gave 2nd 1st, 0.15 g., m. 104°, and 2nd 2nd 0.27 g., m. 106°. The ester is unusually soluble in cold 63% alcohol and the second crops are large, hence the 1st 2nd was recrystallized from 8 cc. 63% alcohol 2 cc. water and gave a crop of crystals which may be called (2nd) 2nd 1st 0.50 g., m. 105.7°, and (2nd) 2nd 2nd 0.10 g., m. 105.8°. The 2nd 2nd and (2nd) 2nd 1st were combined and dissolved in 15 cc. 63% alcohol plus 5 cc. water. This gave (2nd) 3rd 1st 0.58 g., m. 106.1° and (2nd) 3rd 2nd 0.17 g., m. 106.2°. We may take 106° as correct melting point of the ester.

***p*-Hydroxybenzoic Acid.**—The usual mixture of 1 g. of the sodium salt, 1 g. bromide and 15 cc. 63% alcohol was heated for one hour. The ester began to separate almost immediately in such large amount that no attempt was made to keep it in solution. The 1st 1st was 0.87 g., m. 164-74° and 1st 2nd 0.80 g., m. 174°, calculated 1.26 g. As the ester appeared to be very insoluble, even in hot alcohol, 0.20 g. of the 1st 1st was boiled with 60 cc. 95% alcohol and filtered hot. A residue was left on the paper called 2nd 1st 0.06 g., m. 198°. Crystals separated when the solution cooled, 2nd 2nd 0.02 g., m. 195°, and further crystals separated on the addition of water, 2nd 3rd 0.02 g., m. 165–175°. The 2nd 1st was dissolved in 150 cc. boiling 95% alcohol and gave 3rd 1st 0.05 g., m. 198.8°. This was recrystallized from same amount of alcohol and yielded 4th 1st 0.01 g., m. 198.5°. This ester is notable for its extremely slight solubility in even hot strong alcohol. It is best purified by extracting with moderate amounts of hot alcohol before recrystallizing.

m-**Aminobenzoic Acid.**—A mixture of 1 g. of the sodium salt, 1 g. *p*-nitrobenzyl chloride, 15 cc. 63% alcohol was boiled one hour. On cooling an emulsion formed which became crystalline. The 1st 1st was 1.40 g., m. 198° and 1st 2nd 0.12 g., m. 175°, calculated, 1.58 g. The 1st 1st was dissolved in 25 cc. 63% alcohol to which 2 cc. of water was subsequently added. This gave 2nd 1st 0.82 g., m. 198.3° and 2nd 2nd, 0.37 g., m. 198.3°. This ester is yellow.

p-**Aminobenzoic Acid.**—A mixture of 1 g. of the sodium salt, 1 g. of the chloride and 15 cc. 63% alcohol was boiled one hour. A bright yellow precipitate soon began to separate and 30 cc. of 95% alcohol was added, which failed to keep it in solution. The 1st 1st was 0.92 g., and did not melt at 248°. On account of the inconveniently high melting point the preparation was abandoned.

Esters of Dibasic Acids.

Oxalic Acid.—An attempt was made to prepare the mono-ester by boiling 0.6 g. monosodium oxalate with 1 g. *p*-nitrobenzyl chloride and 20 cc. 63% alcohol for one hour. The 1st 1st was 0.95 g., m. 72.5°, unchanged reagent, 1st 2nd, the same.

A mixture of 0.42 g. potassium oxalate, $K_2C_2O_4.H_2O$, 1 g. bromide and 15 cc. 63% alcohol was boiled one hour. Separation of the ester soon took place and 15 cc. 95% alcohol was added, but it was not redissolved. The 1st 1st was 0.15 g., m. 204° and 1st 2nd, 0.10 g., m. 90° (reagent) calculated 0.83 g. Recrystallization from 150 cc. 95% alcohol gave 2nd 1st 0.15 g., m. 204.1°. This was prepared in the former work but the experiment was repeated in the hope of obtaining a better yield. The time of boiling was lengthened and the yield improved. Even here the yield is poor. It is probable that a part of the ester is hydrolyzed to oxalic acid and *p*-nitrobenzyl alcohol.

Ethyl-malonic Acid.—A mixture of 0.5 g. of the disodium salt, 1 g. of the bromide and 15 cc. 63% alcohol was boiled one hour, during which time drops of oil separated. The ester remained an oil after cooling, but solidified in a few hours. The 1st 1st was 0.68 g., m. 74.7° and 1st 2nd 0.15 g., m. 88° (largely reagent), calculated, 0.93 g. The 1st 1st was dissolved in 22 cc. boiling 63% alcohol and gave 2nd 1st 0.65 g., m. 75.2°. and only a trace of 2nd 2nd. Recrystallization from the same amount of alcohol gave 3rd 1st 0.53 g., m. 75.2° and 3rd 2nd only opalescence. This ester is almost completely insoluble in cold 63% alcohol.

Dimethyl-malonic Acid.—A mixture of 0.5 g. of the disodium salt, 1 g. of the bromide and 15 cc. 63% alcohol was boiled one hour. The ester soon began separating as an oil. This solidified on cooling. The

1st 1st was 0.62 g., m. 81° and 1st 2nd 0.09 g., m. 70°, calculated 0.93 g. The 1st 1st was dissolved in 20 cc. boiling 63% alcohol and yielded 2nd 1st 0.62 g., m. 83.5°, 2nd 2nd, unweighable. Recrystallization from 18 cc. of same alcohol gave 0.57 g., m. 83.6°.

Methylethyl-malonic Acid.—A mixture of 0.5 g. of the disodium salt, 1 g. *p*-nitrobenzyl iodide and 15 cc. 63% alcohol was boiled one hour. The ester separated as an oil which solidified after some hours. The 1st 1st was 0.52 g., m. 56°, 1st 2nd, inappreciable. This was recrystallized four times using 20 cc. of 63% alcohol three times and 18 cc. the last time. The results, with melting points, were 2nd 1st 0.45 g., m. 55°, 3rd 1st 0.45 g., m. 55–65°, 4th 1st 0.39 g., m. 66°, 5th 1st 0.30 g., m. 65.6°. All of the second crops were inappreciable. This ester is practically insoluble in cold 63% alcohol.

Isopropyl-malonic Acid.—The mixture consisted of 0.5 g. of the disodium salt, 1 g. of the bromide and 15 cc. 63% alcohol. This was boiled one hour, during which time the ester began to separate as an oil, which solidified on cooling. The 1st 1st was 0.50 g., m. 57°, 1st 2nd, inappreciable, calculated, 0.92 g. Two recrystallizations from 21 cc. 63% alcohol gave 2nd 1st 0.43 g., m. 81.3° and 3rd 1st 0.36 g., m. 81.4°. Only traces were obtained by diluting the mother liquors with water.

Diethyl-malonic Acid.—The reaction mixture was 0.5 g. of the disodium salt, 1.2 g. of the iodide and 15 cc. 63% alcohol. The ester began separating during the hour's boiling. It appeared as an oil which later solidified. The 1st 1st was 0.86 g., m. 89.3°, 1st 2nd unweighable, m. 119.5° (reagent). It was recrystallized twice from 50 cc. 63% alcohol and gave 2nd 1st 0.79 g., m. 91°, and 3rd 1st, m. 91.2°, weight lost. The 2nd 2nd and 3rd 2nd were inappreciable.

Allyl-malonic Acid.—A mixture of 0.8 g. disodium salt, 1 g. bromide and 15 cc. 63% alcohol was boiled 90 minutes. To keep the ester in solution 20 cc. 95% alcohol were added during the boiling. On cooling, an oil separated which solidified after about a week. The 1st 1st was 0.21 g., m. 41°, 1st 2nd, nothing workable. The 1st 1st was recrystallized from 15 cc. 95% alcohol and gave 2nd 1st 0.17 g., m. 43.8°, 2nd 2nd, only trace. Recrystallization from 15 cc. 63% alcohol yielded 3rd 1st 0.07 g., m. 46.1° and again from 10 cc. 63% alcohol, 4th 1st 0.07 g., m. 46°. The 3rd 2nd and 4th 2nd were inappreciable.

Dipropyl-malonic Acid.—The reaction mixture was 0.5 g. of the disodium salt, 12 g. of the iodide, and 15 cc. 63% alcohol. The ester began to separate during the hour's boiling.. The 1st 1st was 0.90 g., m. 117.2°, 1st 2nd, unweighable, m. 123° (reagent), calculated 1.05 g. It was three times recrystallized from 70 cc., 70 cc., and 68 cc., 63% alcohol respectively, and gave 2nd 1st 0.53 g., m. 117.8°, 3rd 1st 0.50 g., m. 118.5°

and 4th 1st m. 118.5° weight lost. All of the second crops were inappreciable.

Benzyl-malonic Acid.—A mixture of 0.6 g. of the disodium salt, 1.2 g. of the iodide and 15 cc. 63% alcohol was boiled one hour. The ester began in 20 minutes to separate as an oil. It solidified on cooling. The 1st 1st was 0.92 g., m. 97.5°, calculated, 1.06 g., 1st 2nd, inappreciable. It was recrystallized from 70 cc. 63% alcohol and yielded 2nd 1st 0.70 g., m. 116°, 2nd 2nd 0.01 g., m. 124° (reagent). The 2nd 1st was heated with 63% alcohol till partially dissolved and the mixture filtered. The residue melted at 119.5° and the crystals from the filtrate at 119.5°. Another recrystallization failed to alter the melting point.

Succinic Acid.—A mixture of 0.35 g. of the disodium salt, 1 g. of the bromide, a slight excess, and 15 cc. 63% alcohol was boiled two hours. During this time 15 cc. more of the alcohol was added. The 1st 1st was 0.38 g., m. 67–74° and 1st 2nd 0.01 g. sticky material, calculated 0.84 g. This was recrystallized from 15 cc. 63% alcohol and gave 2nd 1st 0.18 g., m. 80° and 2nd 2nd 0.04 g., m. 95° (reagent). It was recrystallized three times more, using 10 cc. 63% alcohol each time and the products were 3rd 1st 0.18 g., m. 87.5°; 4th 1st 0.17 g., m. 88.4° and 5th 1st 0.12 g., m. 88.4°.

An attempt was made to prepare the mono-ester. In this 0.65 g. monosodium succinate, 1.2 g. of the iodide, and 15 cc. 63% alcohol were boiled one hour. The ester was sticky at first, but afterwards solidified. The 1st 1st 0.42 g., m 88° and 1st 2nd 0.22 g., m. 87°. The 1st 1st was recrystallized from 12 cc. 63% alcohol and gave 2nd 1st 0.33 g., m. 88.1° and 2nd 2nd 0.01 g., m. 120° (reagent). As the supposed mono-ester melted at the same temperature of the di-ester, a mixed melting point was made of the two and was 88.5° showing the two to be identical.

Monobromosuccinic Acid.—A solution of 0.5 g. of the disodium salt and 1 g. of the bromide in 15 cc. 63% alcohol was boiled one hour. The ester separated out as an oil which did not dissolve on the addition of 15 cc. more of the alcohol. The 1st 1st was 0.37 g., m. 147° and 1st 2nd 0.45 g., m. 55°. It was recrystallized from 40 cc. 63% alcohol plus 30 cc. 95% and yielded 2nd 1st 0.17 g., m. 146.6°, and this, from 40 cc. 95% alcohol, gave 3rd 1st 0.12 g., m. 147.1° and 3rd 2nd 0.01 g., m. 147°.

Dibromosuccinic Acid.—A solution of 0.7 g. of the disodium salt and 1 g. of the bromide in 15 cc. 63% alcohol was boiled, crystal plates separated during the heating and 25 cc. 95% alcohol was added to keep them in solution. The 1st 1st was 0.10 g., m. 154°, 1st 2nd 0.45 g., m. 83°. The 1st 1st was recrystallized four times from 63% alcohol using about 20 cc. 63% alcohol each time. The results were 2nd 1st 0.10 g., m. 168°, 3rd 1st m. 168.5°, 4th 1st m. 168.5°, 5th 1st m. 168.5°. The second crops were negligible.

Maleic Acid.—A solution of 0.6 g. of the disodium salt, 1 g. of the bromide in 15 cc. 63% alcohol was boiled two hours. Another 15 cc. of the alcohol was added during this time to keep the product in solution. On cooling, an oil separated which did not solidify. The mother liquor was poured off and the oil dissolved in 30 cc. hot 63% alcohol. The ester came down as an oil but soon solidified. The 1st 1st was 0.25 g., m. 85.2° and 1st 2nd an oil. It was twice crystallized from 60 cc. 63% alcohol, giving 2nd 1st 0.22 g., m. 89.3° and 3rd 1st 0.15 g., m. 89.3°. The second crops were trifling.

Fumaric Acid.—A mixture of 0.6 g. of the sodium salt and 1 g. of the bromide in 15 cc. 63% alcohol was boiled 90 minutes. A crystalline precipitate soon formed and a little of the sodium salt remained undissolved to the end. The addition of 10 cc. 63% alcohol did not seem to affect the precipitated ester. The 1st 1st was 0.52 g., m. 150.5°, 1st 2nd only an opalescence. Of this 0.1 g. was recrystallized from 55 cc. 95% alcohol and yielded 2nd 1st m. 150.8°. The fumarate is much less soluble than the maleate.

Sebacic Acid.—From a solution of 0.5 g. of the sodium salt and 1 g. of the bromide in 15 cc. 63% alcohol, the ester began to separate during the boiling and was not kept in solution by the addition of 45 cc. 95% alcohol. The ester appeared as an oil, which solidified after a day. The 1st 1st was 0.68 g., m. 69.8° and 1st 2nd 0.12 g., m. 50°, calculated 1.09. The 1st 1st was twice crystallized from 60 cc. 63% alcohol yielding 2nd 1st 0.61 g., m. 72.5° and 3rd 1st 0.57 g., m. 72.6°.

Malic Acid, Mono-ester.—A solution of 0.7 g. monosodium salt and 1 g. of the bromide in 15 cc. 63% alcohol was boiled one hour. The solution remained clear, but gave, on cooling, an emulsion which soon became crystalline. The 1st 1st was 0.30 g., m. 86.5° and 1st 2nd 0.08 g., m. 79°. Two recrystallizations, from 10 cc. 63% alcohol, gave 2nd 1st m. 87° and 3rd 1st 0.20 g., m. 87.2°. The 2nd 2nd and 3rd 2nd were each about 0.01 g. and both melted at 94°, showing them to be impure bromide. This is the only acid ester that, so far, has been obtained.

Malic Acid, Di-ester.—A solution of 0.7 g. of the disodium salt and 1 g. of the bromide in 15 cc. 63% alcohol was boiled one hour. A flocculent precipitate separated from the boiling solution. The 1st 1st was 0.50 g., m. 121.8°. This was recrystallized from 15 cc. 63% alcohol and then from 13 cc. of the same, yielding 2nd 1st 0.28 g., m. 124.6° and 3rd 1st 0.28 g., m. 124.5°. All the second crops were inappreciable.

Tartaric Acid.—Two attempts were made to prepare the mono-ester, but only the unchanged reagent and a trace of the di-ester could be found in the products.

The di-ester was described in the former work but the yield obtained was small. On account of the importance of this acid the preparation was repeated.

A solution of 0.6 g. of the sodium salt, $Na_2C_4H_4O_6.2H_2O$, and 1 g. of the bromide was boiled one hour. The 1st 1st was 0.65 g., m. 154° and 1st 2nd 0.02 g., m. 91°, calculated 0.97 g. The 1st 1st was dissolved in 20 cc. 63% alcohol plus 10 cc. 95% alcohol, and from this was obtained 2nd 1st 0.37 g., m. 163° and 2nd 2nd 0.08 g., m. 100°. It was recrystallized from 35 cc. 63% alcohol and gave 3rd 1st 0.37 g., m. 162.7°, 3rd 2nd, nothing. This 162.7° agrees closely with 163° previously found.

Racemic Acid.—A solution of 1 g. disodium racemate and 1 g. of the bromide in 15 cc. 63% alcohol was boiled two hours. The 1st 1st was 0.50 g., m. 145° and 1st 2nd 0.05 g., m. 75–98°. Two recrystallizations from 10 cc. 63% alcohol gave 2nd 1st 0.33 g., m. 148° and 3rd 1st 0.32 g., m. 147.6°. Both 2nd 2nd and 3rd 2nd were inappreciable.

Phthalic Acid.—A solution of 0.6 g. of the disodium salt and 1 g. of the chloride in 15 cc. 63% alcohol was boiled 90 minutes. The ester separated during the heating and 40 cc. of the same alcohol was added. The 1st 1st was 0.17 g., m. 152° and 1st 2nd 0.53 g., m. 72° (reagent). The 1st 1st was twice recrystallized from 50 cc. 95% alcohol, giving 2nd 1st 0.17 g., m. 155° and 3rd 1st 0.17 g., m. 155.5°. The mother liquors gave only an opalescence on dilution with water.

Isophthalic Acid.—The reaction mixture was as in the above. The addition of 50 cc. 95% alcohol did not prevent the separation of the ester from the boiling solution. The 1st 1st was 0.10 g. but it did not melt at 255°, so it was abandoned.

Laevulinic Acid and **Mucic Acid** were tried, but the esters were not obtained.

The results are brought together in tabular form, the second and third columns giving the weights of the first and second crops of crystals. When the 1st 2nd seemed to be mainly unchanged reagent, its weight is put in parenthesis and is not used in calculating the total yield. In the sixth and seventh will be found the first and final melting points. The eighth column gives the strength of alcohol used for recrystallizations, and the ninth, the number of cubic centimeters of boiling alcohol used, calculated for 1 gram of the ester. These figures are only approximate solubilities as the esters could have been dissolved in somewhat less alcohol, some of them, doubtless, in much less. In the last column is given the volume of the alcohol when cold that would be required to dissolve 1 gram of the ester. This is calculated from the amount of ester precipitated by water. In the cases where figures are not given, the solubility of the esters in cold 63% alcohol is extremely small. The symbol Cl, Br, or I in the first column indicates the *p*-nitrobenzyl halide used in each preparation.

TABLE I.—YIELDS, MELTING POINTS, AND APPROXIMATE SOLUBILITIES OF *p*-NITROBENZYL ESTERS.

Acid.	Halide.	1st 1st. G.	1st 2nd. G.	Total. G.	Calc. G.	Melting point.		Alcohol. %.	Hot. Cc.	Cold. Cc.
						First.	Final.			
Thiocyanic......	Cl	1.15	0.07	1.22	1.13	83.3°	85°	63	9	750
Phenylacetic.....	Br	1.25	0.02	1.27	1.25	63.8°	65°	63	20	830
Cinnamic........	Br	1.15	..	1.15	1.31	116.8°	116.7°	63	70	..
Hydrocinnamic..	Br	0.93	..	0.93	1.32	32°	36.3°	63	21	..
Hippuric........	Br	1.18	(0.02)	1.18	1.45	136°	136°	63	12	750
m-Toluic........	Cl	0.93	(0.23)	0.93	1.59	84°	86.6°	63	32	1000
Salicylic.........	Br	0.93	0.05	0.98	1.26	96.5°	96.3°	63	37	..
m-Hydroxybenzoic	Br	0.55	0.60	1.15	1.26	106°	106.1°	63	31	60
p-Hydroxybenzoic	Br	0.87	0.08	0.95	1.26	164°	198.5°	95	430	3000
m-Aminobenzoic.	Cl	1.40	0.12	1.52	1.58	198°	198.3°	63	18	68
p-Aminobenzoic..	Cl	0.92	..	0.92	1.59	>248°	..	..	..	..
Oxalic..........	Cl	0.15	(0.10)	0.15	0.83	204°	204.1°	95	1000	..
Ethyl-malonic...	Br	0.68	(0.15)	0.68	0.92	74.7°	75.2°	63	32	..
Dimethyl-malonic	Br	0.62	0.09	0.71	0.92	81°	83.6°	63	32	..
Methyl-ethyl-malonic.........	Br	0.52	..	0.52	0.79	56°	65.6°	63	40	..
Isopropyl-malonic	Br	0.50	..	0.50	0.92	57°	81.4°	63	42	..
Diethyl-malonic...	I	0.86	..	0.86	0.94	89.3°	91.2°	63	58	..
Allyl-malonic....	Br	0.21	..	0.21	0.91	41°	46°	95	71	..
Dipropyl-malonic	I	0.90	..	0.90	1.05	117.2°	118.5°	63	123	..
Benzyl-malonic..	I	0.92	..	0.92	1.06	97.5°	119.5°	63	76	..
Succinic.........	I	0.38	0.01	0.39	0.88	64–74°	88.4°	63	40	..
Bromosuccinic...	Br	0.37	(0.45)	0.37	1.08	147°	147.1°	77	190	..
Dibromosuccinic.	Br	0.10	(0.45)	0.10	1.26	154°	168.5°	82	500	..
Maleic..........	Br	0.25	..	0.25	0.89	85.2°	89.3°	63	240	..
Fumaric.........	Br	0.52	..	0.52	0.89	150.5°	150.8°	95	550	..
Sebacic.........	Br	0.68	0.12	0.80	1.09	69.8°	72.6°	63	88	..
Malic, mono-ester	Br	0.30	(0.08)	0.30	1.25	86.5°	87.2°	63	33	1000
Malic, di-ester...	Br	0.50	..	0.50	0.93	121.8°	124.5°	63	30	..
Tartaric.........	Br	0.65	(0.02)	0.65	0.97	154°	162.7°	72	46	350
Racemic........	Br	0.50	(0.05)	0.50	0.97	145°	147.6°	63	20	..
Phthalic.........	Cl	0.17	(0.53)	0.17	1.26	152°	155.5°	95	300	..
Isophthalic......	Cl	0.10	..	0.10	1.26	>255°	..	..	..	..

Discussion of Results.

It appears that *p*-nitrobenzyl chloride, bromide, and iodide can all be used. With *m*-toluic acid, the chloride gave only 62% of the calculated amount of ester, while in previous work 97% was obtained from *o*-toluic acid, using the bromide. In this case a considerable amount of unchanged chloride was recovered, showing that the chloride does not react as promptly as is desirable. The results for diethyl-malonic, dipropyl-malonic and benzyl-malonic, with which the iodide was used, are better than those obtained for other substituted malonic acids with the bromide. This suggests that it might be advantageous to use the iodide, rather than the bromide, for dibasic acids. As the di-*p*-nitrobenzyl esters of dibasic acids are very insoluble, it is easy to purify them from any unchanged iodide.

Esters of three acids, thiocyanic, oxalic and tartaric, appear here as well as in the former work. There is close agreement in the melting points found, but the estimates of solubilities differ, though they are of the same order in all cases.

Summary.

By the use of reagent and methods previously outlined, *p*-nitrobenzyl esters of a number of acids have been prepared and their melting points determined.

The following *p*-nitrobenzyl esters have been prepared:

p-Nitrobenzyl phenylacetate, $C_6H_5CH_2CO_2.CH_2C_6H_4NO_2$, m. 65°;

Cinnamate, $C_6H_5CH:CHCO_2.CH_2C_6H_4NO_2$, m. 116.7°;

Hydrocinnamate, $C_6H_5CH_2CH_2CO_2.CH_2C_6H_4NO_2$, m. 36.3°;

Hippurate, $C_6H_5CONHCH_2CO_2.CH_2C_6H_4NO_2$, m. 136°;

m-Toluate, $CH_3C_6H_4CO_2.CH_2C_6H_4NO_2$, m. 86.6°;

Salicylate, $HOC_6H_4CO_2.CH_2C_6H_4NO_2$, m. 96.3°;

m-Hydroxybenzoate, $HOC_6H_4CO_2.CH_2C_6H_4NO_2$, m. 106.1°;

p-Hydroxybenzoate, $HOC_6H_4CO_2.CH_2C_6H_4NO_2$, m. 198.5°;

m-Aminobenzoate, $NH_2C_6H_4CO_2.CH_2C_6H_4NO_2$, m. 198.3°;

p-Aminobenzoate, $NH_2C_6H_4CO_2.CH_2C_6H_4NO_2$, m. above 250°;

Oxalate, $(.CO_2.CH_2C_6H_4NO_2)_2$, m. 204.1°;

Ethyl-malonate, $C_2H_5CH(CO_2.CH_2C_6H_4NO_2)_2$, m. 75.2°;

Dimethyl-malonate, $(CH_3)_2C(CO_2.CH_2C_6H_4NO_2)_2$, m. 83.6°;

Methylethyl-malonate, $CH_3(C_2H_5)C(CO_2.CH_2C_6H_4NO_2)_2$, m. 65.6°;

Isopropyl-malonate, $(CH_3)_2CH.CH(CO_2.CH_2C_6H_4NO_2)_2$, m. 81.4°;

Diethyl-malonate, $(C_2H_5)_2C(CO_2.CH_2C_6H_4NO_2)_2$, m. 91.2°;

Allyl-malonate, $CH:CHCH_2CH(CO_2.CH_2C_6H_4NO_2)_2$, m. 46°;

Dipropyl-malonate, $(C_3H_7)_2C(CO_2.CH_2C_6H_4NO_2)_2$, m. 118.5°;

Benzyl-malonate, $C_6H_5CH_2CH(CO_2.CH_2C_6H_4NO_2)_2$, m. 119.5°;

Succinate, $(.CH_2CO_2.CH_2C_6H_4NO_2)_2$, m. 88.4°;

Bromosuccinate, $C_2H_3Br(CO_2.CH_2C_6H_4NO_2)_2$, m. 147.1°;

Dibromosuccinate, $C_2H_2Br_2(CO_2.CH_2C_6H_4NO_2)_2$, m. 168.5°;

Maleate, $(:CHCO_2.CH_2C_6H_4NO_2)_2$, m. 89.3°;

Fumarate, $(:CHCO_2.CH_2C_6H_4NO_2)_2$, m. 150.8°;

Sebacate, $(.CH_2CH_2CH_2CH_2CO_2.CH_2C_6H_4NO_2)_2$, m. 72.6°;

Malate, mono-$HCO_2CH_2CH(OH)CO_2.CH_2C_6H_4NO_2$, m. 87.2°;

Malate, di-$C_2H_4O(CO_2CH_2C_6H_4NO_2)_2$, m. 124.5°;

Racemate, $(.CH(OH)CO_2.CH_2C_6H_4NO_2)_2$, m. 147.6°;

Phthalate, *o*-$C_6H_4(CO_2.CH_2C_6H_4NO_2)_2$, m. 155.5°;

Isophthalate, *m*-$C_6H_4(CO_2.CH_2C_6H_4NO_2)_2$, m. above 250°.

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