However, for the benefit of any who are using, or may consider using this substance, I would call attention to an advisable precaution in its preparation. A saturated solution of the acid phthalate on chilling will deposit crystals of a more acid salt, having the formula, $2KHC_8H_4O_4.C_8H_6O_4$. These crystals are in the form of prismatic needles, easily distinguished under the microscope from the 6-sided orthorhombic plates of the salt, $KHC_8H_4O_4$. A contamination of the acid phthalate with this "triphthalate" would be fatal for its use as a standard, but the formation of the latter can be entirely avoided by crystallization at temperatures above 20°.

The writer hopes soon to present the results of a detailed chemical and crystallographic study of the acid phthalates, which has proved interesting in various ways. F. D. DODGE.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY.]

THE ACTION OF ACETIC ANHYDRIDE ON ALPHA NAPHTHYL PROPIOLIC ACID.[1]

BY BYRON L. WEST.

Received February 7, 1920.

Introduction.

Over twenty years ago, Michael and Bucher[2] found that phenyl propiolic acid, when treated with acetic anhydride, yields α-phenylnaphthalene-2,3-dicarboxylic anhydride. This compound was unexpected, and its identity was unknown for almost 2 years. In a previous research[3] they found that acetic anhydride reacts with acetylene dicarboxylic acid to form the anhydride of acetoxyl-maleic acid; and on treating this anhydride with water, they obtained oxalacetic acid. If acetic anhydride would act on phenyl propiolic acid in an analogous manner, the anhydride of β-acetoxyl-cinnamic acid would be formed, and this compound, on treatment with water, would yield β-hydroxycinnamic acid.

Their explanation of the unexpected formation of the α-phenylnaphthalene derivative may be best explained by the following formulas.

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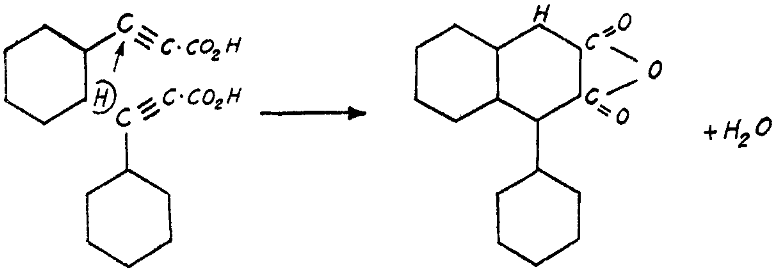
[1] This is an abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Brown University by the holder of the Morgan Edwards Fellowship founded by the Philadelphia Alumni of Brown University. The investigation was conducted in the Chemical Laboratory of Brown University at the suggestion and under the personal direction of Professor John E. Bucher. The author wishes to express his gratitude to Doctor William Williams Keen, President of the Philadelphia Alumni, for his constant and helpful interest and encouragement.

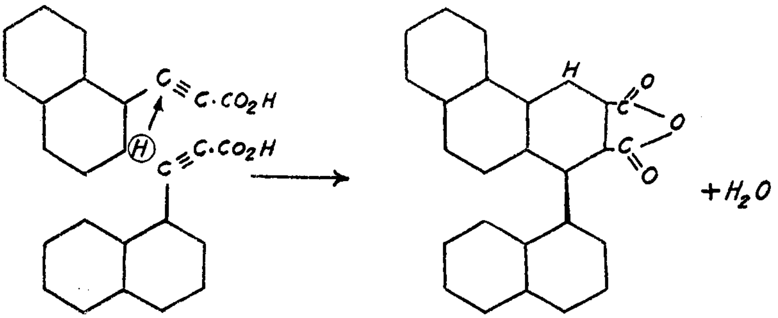
[2] Michael and Bucher, *Am. Chem. J.*, **20**, 89 (1898).

[3] *Ber.*, **28**, 2511 (1895).



It will be seen that their explanation is based on the fact that the *ortho* hydrogen atom of the first molecule of the phenyl propiolic acid wanders to the β-carbon atom of the same molecule. The β-carbon atom of the second molecule unites with the *ortho* carbon atom of the first molecule from which the hydrogen wandered, and the 2 α-carbon atoms of the side chains unite to complete the naphthalene ring.

This reaction has been found to hold for phenyl propiolic acids in general, and the following substituted phenyl propiolic acids polymerize with the above treatment to their corresponding α-phenyl-naphthalene-2,3-dicarboxylic anhydrides: *o*-chloro-, *o*-bromo-, *m*-nitro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, *p*-methyl-, and a number of other phenyl propiolic acids. It has been further shown by Holt[1] that symmetrical tribromophenyl propiolic acid is not condensed to a naphthalene derivative by the action of acetic anhydride, the anhydride of the bromo acid only being formed. The reason for this is apparently that the 2 *ortho* bromine atoms are held too firmly for either to wander from the nucleus, as would be necessary if a similar condensation took place. However, Foote[1] was unable to obtain any condensation product from β-anthraquinoyl propiolic acid where there were 2 hydrogen atoms on the nucleus. He explained the result by showing that his acid decomposed at 135°.



The purpose of this investigation has been to determine whether this interesting condensation, which seems general for propiolic acids of the phenyl series, could be extended to the naphthalene series as well. If

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[1] Unpublished researches.

an analogous condensation should take place, the product would be an α-naphthyl-phenanthrene di-carboxylic anhydride, as shown by the preceding formulas.

Previous Methods of Preparing α-Naphthyl Propiolic Acid.

A new and satisfactory method for obtaining α-naphthyl propiolic acid from the present limited supplies of chemicals was first worked out. The action of acetic anhydride on this acid was then investigated. In a manner analogous to that of Glaser[1] who prepared phenyl propiolic acid by treating potassium phenyl acetylene with carbon dioxide under pressure, Leroy[2] prepared α-naphthyl propiolic acid with poor and uncertain yields from potassium naphthyl acetylene and carbon dioxide. However, just as in the phenyl series, this method did not seem to us feasible for obtaining the acid in large quantities. Moreover, there is room for doubt as to whether Leroy ever obtained an absolutely pure acid uncontaminated by its β-isomer. He prepared his α-naphthyl ketone (from which he obtained his acetylene derivative) by the method of Claus and Feist,[3] and Pampel and Schmidt.[4] In this method acetyl chloride and naphthalene are condensed with aluminum chloride. In 1889, Müller and Pechman[5] performed this same Freidel and Crafts reaction and obtained a ketone that differed widely in properties from that described in either of the 2 articles published; they called their product the β-ketone. Claus and Terstegen[6] attempted to explain the differences and said that the experiment at higher temperatures gave an α- and at lower temperatures a β-ketone. In 1896, however, 5 years after Leroy's article on the propiolic acid preparation, was published Rousset[7] stated that none of these authors had succeeded in isolating the ketones and obtaining them pure. He found it necessary to form their picrates in order to separate the 2 isomers.

Bucher[8] prepared many of the propiolic acids mentioned previously from the corresponding cinnamic acids. They made the cinnamic ester dibromide and heated the latter with alcoholic potash. The value of this method depends on the ease with which the corresponding aldehydes can be obtained from which the cinnamic acids are prepared by means of the Perkins synthesis. However, a satisfactory method of preparation for α-naphthaldehyde was not available. Methyl naphthalene cannot be obtained without great expense. Furthermore,

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[1] *Ann.*, **154**, 140 (1870).

[2] Leroy, *Bull. soc. chim.*, [3] **7**, 644 (1891).

[3] Claus and Feist, *Ber.*, **19**, 3180 (1886).

[4] Pampel and Schmidt, *ibid.*, **19**, 2898 (1886).

[5] Müller and Pechman, *ibid.*, **22**, 2561 (1889).

[6] Claus and Terstegen, *J. prakt. Chem.*, **50**, 517 (1894).

[7] Rousset, *Bull. soc. chim.*, [3] **17**, 58 (1896).

[8] Bucher, *Am. Chem. J.*, **32**, 212 (1910).

Scherler[1] in attempting to halogenate the side chain, found that the chlorine or bromine atoms are just as liable to replace the hydrogens on the ring as those on the side chain.

The usual method for obtaining aldehydes which involves heating the calcium salt of α-naphthoic acid with calcium formate, yields mostly naphthalene and only faint traces of the aldehyde.[2] Gatterman and Maffezzoli[3] have prepared α-naphthaldehyde by use of the Grignard reaction from magnesium bromo-naphthalene and an excess of formic ester. Owing to the difficulties involved and because of a desire to use only comparatively inexpensive and easily obtainable materials, this method has not been used. Rousset[4] obtained α-naphthaldehyde from the corresponding naphthyl-glyoxylic acid. In obtaining this acid he had to separate the α- and β-isomers, and this proved difficult.

The best known method for obtaining α-naphthaldehyde has been described by Brandis[5] as a long, tedious "time-consuming process" with poor yields. It is that of Bamberger and Lodter[6] and consists of the reduction of the thioamide to the methyl amine and the subsequent changing of this product to the naphthyl-methyl alcohol which in turn is oxidized to the aldehyde.

It appeared, therefore, the problem was to be solved either by (1) devising a method for obtaining α-naphthyl propiolic acid without the use of the aldehyde as a starting point, or by (2) discovering more efficient means for the preparation of α-naphthaldehyde.

Considerable time and effort was spent on the first of these 2 possibilities in an attempt to prepare the propiolic acid from α-naphthyl acetic ester. This work was discontinued because of the success of the following method.

New Method for Obtaining α-Naphthaldehyde.—Guereschi[7] prepared benzyl alcohol by reducing benzamid in a hydrochloric acid and water containing ether solution. Later Hutchinson[8] prepared *o*-toluyl alcohol in an analogous manner from *o*-toluic amide, using 15% alcohol instead of ether. His yield was 40–45%. In this laboratory, Barnard in investigating Guereschi's work, increased the latter's yield from 31.5% to 56% by the use of 95% alcohol.

α-Naphthoic amide is very readily prepared, as is well known, and its

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[1] Scherler, *Ber.*, **24**, 3927 (1891).

[2] Bamberger and Lodter, *ibid.*, **21**, 259 (1888).

[3] Gatterman and Maffezzoli, *ibid.*, **36**, 4152 (1903).

[4] Rousset, *Bull. soc. chim.*, [3] **17**, 313 (1896).

[5] Brandis, *Ber.*, **22**, 2153 (1889).

[6] Bamberger and Lodter, *ibid.*, **21**, 259 (1888).

[7] Guereschi, *ibid.*, **7**, 1462 (1874).

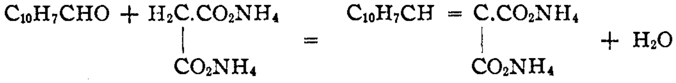
[8] Hutchinson, *ibid.*, **24**, 175 (1891).

several methods will be discussed later. The most feasible was that of Hoffman[1] who obtained it directly from the nitrile.

By use of a mechanical stirrer, α-naphthamide was successfully reduced in 95% alcohol solution with 4% sodium amalgam and commercial hydrochloric acid to α-naphthyl-methyl alcohol and yields of 70% obtained with several 100 g. lots.

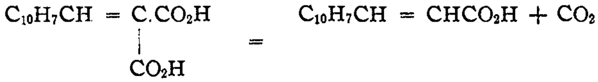
The alcohol was readily oxidized to the aldehyde by the use of sodium dichromate and dil. sulfuric acid following a method similar to that of Bamberger and Lodter.[2]

Perkin's well known synthesis was used by Brandis[3] and Lugli[4] and Rousset[5] to obtain the acrylic acid. The yields at best were only 45 to 50% of the theory after 50 to 60 hours heating and the product was exceedingly difficult to purify. The malonic acid synthesis used by Knoevenagel[6] on benzaldehyde to obtain benzal malonic acid and from it the cinnamic acid gave much better results. The reaction completed itself in a few hours and gave a comparatively very pure product. The method consists of heating one molecule of α-naphthaldehyde and one molecule of malonic acid with 2 molecules of an 8% alcoholic ammonia solution



$$C_{10}H_7CHO + \begin{array}{c} H_2C.CO_2NH_4 \\ | \\ CO_2NH_4 \end{array} = \begin{array}{c} C_{10}H_7CH = C.CO_2NH_4 \\ \qquad\qquad | \\ \qquad\qquad CO_2NH_4 \end{array} + H_2O$$

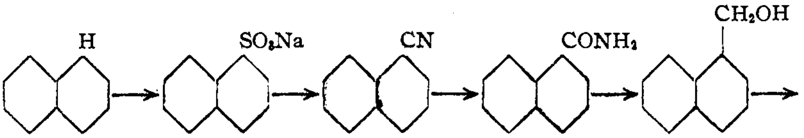
On acidification the naphthal malonic acid was readily changed to the acrylic acid on heating.



$$\begin{array}{c} C_{10}H_7CH = C.CO_2H \\ \qquad\qquad | \\ \qquad\qquad CO_2H \end{array} = C_{10}H_7CH = CHCO_2H + CO_2$$

From this compound the method of Michael and Bucher was successfully used to obtain the α-naphthyl propiolic acid. The acrylic ester dibromide was readily made and the subsequent treatment with alcoholic potash (3 molecules) yielded the α-naphthyl propiolic acid.

The whole synthesis follows



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[1] Hoffman, *Compt. rend.*, **66**, 486 (1868).

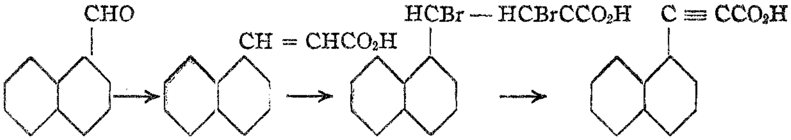
[2] *Loc. cit.*

[3] Brandis, *Ber.*. **22**, 2153 (1889).

[4] Lugli, *Gazz. chim. ital.*, **11**, 393 (1881).

[5] Rousset, *Bull. soc. chim.*, [3] **17**, 813 (1896).

[6] Knoevenagel, *Ber.*, **31**, 2604 (1898).



This synthesis proved very interesting, for the pure halogen-free propiolic acid was obtained by forming of the more soluble ammonium salt by means of ammonium carbonate. A final recrystallization from carbon tetrachloride yielded the product pure in well-formed needles.

The next step, after the acid had been obtained and identified, was to boil it with acetic anhydride in a manner similar to that of Michael and Bucher. The possible outcome has been briefly reviewed and the results of the experiments are reserved until the explanation of the experimental part and the final conclusion.

Experimental Part.

Sodium Salt of α-Naphthalene Sulfonic Acid.—Commercial naphthalene was used in forming the α-sulfonic acid. The standard method of preparation need not here be described. The sulfonation was carried out below 60° and any β-isomer was removed when the calcium salt was made. Treating this with sodium carbonate readily yielded the sodium salt of α-naphthalene sulfonic acid.

Alpha Naphtho Nitrile.[1]—Fifty g. of potassium cyanide was first finely ground and then mixed and intimately ground with 100 g. of pulverized sodium α-naphthalene sulfonate which had been dried at 200°. The whole charge was placed in an iron retort and slowly distilled by heating gradually and increasing the heat toward the end to a dull red. Yields averaged 55–57 g. of crude nitrile. Several hundred g. was obtained by repeating this experiment.

Purification of the Nitrile.—Attempts to obtain pure naphthoic amide directly from the crude nitrile yielded an impure product discolored by a tarry substance, the solubility of which in alcohol was about the same as the amide itself. This impurity is fluorescent in alcohol. As is well known, one of the chief impurities in this crude nitrile is naphthalene which is readily volatile in steam at 100°, while the nitrile is practically non-volatile at this temperature. Consequently, 200 g. of the impure nitrile was distilled with steam until the odor of naphthalene was no longer discernible in the distillate. The temperature of the steam was raised by means of a superheater and the nitrile was readily distilled at 195° to 200°, coming over with an equal volume of water, as a slightly yellow oil which when cooled with ice water soon solidified to a white cake. At the end of the distillation a more difficultly volatile substance solidified in the condenser. This was discarded with the residue in the

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[1] Merz and Mühlhauser, *Ber.*, 3, 709 (1870).

flask. The pure nitrile thus obtained melted at 37–38°. Yield, 154 g.

α-Naphthamide. (*1*) *Hydrogen Peroxide Method.*—Analogous to the method of Radnozewski[1] who prepared benzamide from benzo-nitrile in quantitative yields by the use of alkaline hydrogen peroxide, 2.5 g. of the nitrile was added to a 3% solution of hydrogen peroxide made alkaline with caustic soda. The temperature was maintained at 40° and on vigorous shaking the oily drops soon solidified. The amide, recrystallized from alcohol, showed the yield to be practically quantitative. However, for preparation on a large scale, because of the expense of the process and the difficulty of keeping the amide formed from occluding unchanged nitrile, this method was not used. The yield was quantitative. M. p. 202°.

(*2*) *Sodium Hydroxide Method,* $C_{10}H_7CN + H_2O = C_{10}H_7CONH_2$.—Forty g. of sodium hydroxide was dissolved in 400 cc. of 95% alcohol and filtered into a flask containing 150 g. of pure α-naphtho-nitrile. The flask was provided with a return condenser, heated for 1/2 hour and cooled. The large crop of crystals of amide which resulted was filtered off and washed with alcohol. The filtrate was again boiled for 1/2 hour as before, and a second crop of crystals was obtained. The process was repeated a third time. After a thorough washing with water to remove all sodium naphthoate, the amide existed as pure white glassy needles. Yield, 100 g.; m. p. 203° (uncorr.).

The filtrates and washings were combined and from them the theoretical quantity of α-naphthoic acid not obtained as amide was recovered.

(*3*) *Amide from Acid,*

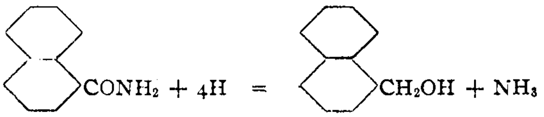
$$C_{10}H_7COOH + PCl_5 = C_{10}H_7COCl + POCl_3 + HCl$$

$$C_{10}H_7COCl + 2NH_3 = C_{10}H_7CONH_2 + NH_4Cl.$$

Seventy-five g. of naphthoic acid was dissolved in 375 g. of carbon tetrachloride in a flask provided with a return condenser. To this was added, in small quantities, 91 g. of phosphorus pentachloride. After the last addition, the flask was heated on a water-bath until no more hydrogen chloride was evolved. The product was then cooled with ice and saturated with dry ammonia. Finally an excess of ammonium hydroxide (sp. gr. 0.9) was added and the carbon tetrachloride was recovered by distillation. The amide was filtered off and washed with water and a little alcohol. Yield of pure white amide, 50 g.

From the filtrate, the unchanged acid was recovered.

α-Naphthyl-methyl Alcohol,



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[1] Radnozewski. *Ber.*, 18, 355 (1885).

Eighty-three g. of α-naphthamide was dissolved in 1500 g. of 95% alcohol in a large battery jar. To this 57.6 cc. of 28% hydrochloric acid was added, theoretically the amount necessary to form the hydrochloride of the amide. The apparatus was provided with a mechanical stirrer. It was found to be very important to have this stirrer project almost to the bottom of the jar in order that the mercury and the liquid amalgam subsequently present might be thoroughly stirred up and the most efficient contact with the solution obtained.

4500 g. of a 4% sodium amalgam was added gradually at the rate of 100 g. every 15 minutes. Each hundred g. of amalgam was accompanied by the addition of 20.5 cc. of 28% hydrochloric acid. This was a molecular equivalent of the amount of amalgam and kept the acidity of the solution almost constant. 980 cc. of 28% hydrochloric acid was required.

After the last addition had been made, the stirring was allowed to continue for 30 to 45 minutes. The solution was next made alkaline with caustic soda, filtered from sodium chloride and mercury and the ethyl alcohol was distilled off on a water bath. On the surface of the liquid in the flask the crude α-naphthyl-methyl alcohol appeared as a light brown oil which soon solidified on cooling. The readily soluble naphthyl-methyl alcohol was easily separated from unchanged amide and other impurities by grinding up this cake in a mortar with a little ether and filtering. The ether was distilled off and the crude α-naphthyl-methyl alcohol was obtained. Yield, 46 g., 63%. M. p. 58–60°.

Thirty-two g. of amide was recovered, m. p. 188°. When recrystallized the m. p. was 202°.

Distillation.—Distilled at 10 mm. pressure, the boiling point was 193° and the distillate was a clear, almost colorless oil which solidified to pure white needles on cooling. M. p. 57–60°. Bamberger and Lodter[1] gave m. p. 59.5° and b. p. 301° at 715 mm.

α-Naphthaldehyde.[2]—After the last traces of ether, alcohol and water had been removed by distillation *in vacuo* on a water bath, 44 g. of the crude α-naphthyl-methyl alcohol was suspended in 330 cc. of 20% sulfuric acid. 10% of impurities was allowed for in calculating for the amount of sodium dichromate to be used which thus was found to be 25 g. This was dissolved in 330 cc. of water. The flask was vigorously shaken to form an emulsion of the aromatic alcohol in the acid, and the dichromate solution was added a few cc. at a time. Bamberger and Lodter added the solid dichromate, but this method did not work as well and gave lower yields. As the oxidation progresses, a very characteristic, penetrating aldehyde-like odor is emitted. After the last addition of the dichromate solution, the contents of the flask is quickly cooled and washed

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[1] *Loc. cit.*

[2] Bamberger and Lodter, *loc. cit.*

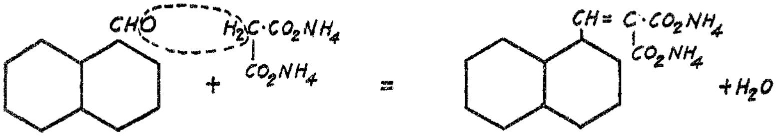
out and extracted with ether. After washing the extract with sodium carbonate solution and finally with water, the ether was distilled off and the product cooled. It was immediately stirred up with a freshly prepared saturated solution of sodium hydrogen sulfite and suddenly solidified to a yellowish cake. An excess of bisulfite solution was next added and the cake was stirred up to the form of a paste which was kept in the refrigerator overnight.

This aldehyde addition product was filtered and washed with alcohol and ether, and finally was ground up with ether in a mortar and washed and filtered again. It was then dried *in vacuo*. Yield, 36 g. of addition product plus some sodium hydrogen sulfite, or 17 g. of aldehyde, equivalent to 42%.

Oxidation to Naphthoic Acid.—A small quantity of the addition product was dissolved in water and treated with sodium carbonate solution. The product was then extracted with ether, which on evaporation yielded an oil that had a characteristic, penetrating, aldehyde-like odor. After standing exposed to the air, it soon lost its odor and crystallized. These crystals readily dissolved in sodium carbonate solution, and on acidifying the solution, were thrown out as a white precipitate. M. p. 158°. Pure α-naphthoic acid melts at 160°.

α-Naphthyl-acrylic Acid. (*1*) *Perkin's Synthesis.*[1]—The usual Perkin's synthesis as described in the literature was tried and various amounts of potassium acetate and acetic anhydride were used, with no improvement in the yield. Long heating (50–60 hours) was necessary and the product obtained was difficultly purified from tarry impurities. Yield, 45%.

(*2*) *α-Naphthyl-malonic Acid Method,*



The aldehyde itself was prepared from the addition product by dissolving 12.5 g. of the bisulfite compound in water (and filtering if any remained undissolved). The solution was then treated with an excess of sodium carbonate solution and finally was extracted with ether. After being washed with water, the ether extract was placed in a tared flask from which the ether was distilled off on a boiling-water bath and last traces removed *in vacuo*, which would leave the aldehyde free from any dissolved water or alcohol. After cooling, the flask was weighed and to the aldehyde (69) was added 6 g. of malonic acid. 24.4 cc. of 8% alcoholic ammonia was then added to the mixture slowly. The flask

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[1] Brandis, *Ber.*, **22**, 2153 (1889); Lugli, *Gazz. chim. ital.*, **11**, 393 (1881); Rousset, *Bull. soc. chim.*, [3] **17**, 813 (1896).

was cooled and vigorously shaken and soon the mixture became a crystalline paste. The flask was now provided with a return condenser and was heated on a water bath for 30 minutes, when all the crystals went into solution. Then the alcohol was distilled off and the last traces removed *in vacuo*. The product now existed as a slightly yellow cake.

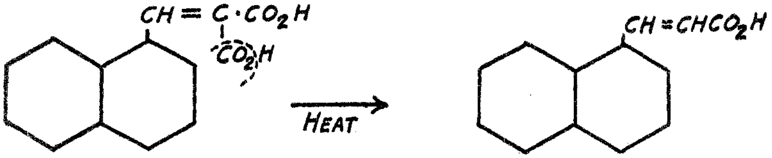
Save for a slight amount of tar, this solid was almost entirely soluble in water containing strong ammonia. A benzene extraction readily left the water solution clear after a filtration through a water-moistened filter paper.

The acid, precipitated with an excess of dil. sulfuric acid, filtered and washed free from mineral acid, was a white solid. The filtrate was evaporated to recover the slight amount of the acid which had shown itself to be slightly soluble in water.

Yield, 4.9 g., m. p. 185–187° with the evolution of carbon dioxide.

0.2762 g. of acid was titrated and required 0.0797 g. of sodium hydroxide. This value would indicate a molecular weight of 278 for a dibasic acid or 139 for a mono-basic acid. Naphthyl-malonic acid has a molecular weight of 242, while that of naphthyl-acrylic acid is 198. The obtained value would be correct for 65% malonic and 35% acrylic acids.

α-Naphthyl-acrylic Acid.—4.1 g. of the α-naphthyl-acrylic malonic acid mixture was heated on an oil bath at 210° to 215° for one hour. The product entirely melted at 190° with the evolution of a gas which gave a test for carbon dioxide. The residue soon crystallized on cooling and was a slightly colored mass of well formed needles that melted at 209–212°. Beautiful needles sublimed and clung to the neck of the flask. These melted at 207.5°. Yield, 3.54 g. From the aldehyde this is a 55.6% yield, a great improvement over Perkin's synthesis when the purity of the product is considered.

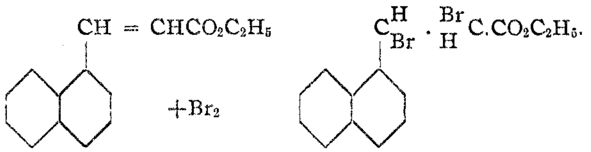


Oxidation of the Acrylic Acid.—To a cold sodium carbonate solution of a small amount of the acrylic acid, dil. potassium permanganate solution was added and was immediately decolorized. An excess was added and the test-tube was heated. The distinct odor of α-naphthaldehyde was very noticeable. When extracted with ether, an oily residue was left on evaporation of the ether. Saturated sodium hydrogen sulfite solution formed an addition product with this oil. After standing in the air the oil soon lost its aldehyde-like odor, and crystals were formed which dissolved in dil. sodium carbonate solution and were reprecipitated on acidifying the solution. This oxidation reaction of acrylic acids to lower aldehydes seems to be general for aromatic acrylic acids.

α-Naphthyl-acrylic Ester.—3.54 g. of α-naphthyl-acrylic acid was added to a flask containing a mixture of 36 g. of absolute alcohol and 4 cc. of conc. sulfuric acid (sp. gr. 1.84). The flask was provided with a return condenser and was heated for 8 hours on a water bath. One-half of the alcohol was then distilled off and the product was poured over finely ground ice to which had been added a solution of sodium carbonate just sufficient to neutralize both acids at the start of the esterification. The ester was quickly extracted with ether, washed with a little water and placed in a tared flask from which the ether was distilled and the last traces of alcohol and water removed *in vacuo* by heating on a water bath. The ester was a slightly brown viscous oil. Yield, 3.54 g., or 89%.

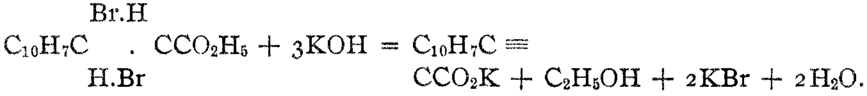
The unchanged acrylic acid was recovered.

α-Naphthyl-α,β-dibromo-acrylic Ester,



To a flask containing 3.54 g. of the acrylic ester 10 cc. of carbon disulfide was added. 25.05 g. of a 10% bromine solution in carbon disulfide was added from a dropping funnel while the flask was being vigorously shaken. The bromination was conducted in the sunlight and was hastened by the acid of a concave mirror. As each drop of the bromine solution struck the surface, it was almost immediately decolorized. The flask was allowed to stand in the sunlight after all of the bromine had been added. Then the carbon disulfide was distilled off and was only slightly pink colored from the trace of unchanged bromine. The ester dibromide soon solidified on standing.

α-Naphthyl-propiolic Acid,



$$C_{10}H_7\overset{Br.H}{\underset{H.Br}{C\quad .}}\ CCO_2H_5 + 3KOH = C_{10}H_7C \equiv CCO_2K + C_2H_5OH + 2KBr + 2H_2O.$$

5.7 g. of the ester dibromide was dissolved in 45 cc. of 95% alcohol and 15.6 cc. of a 15.9% alcoholic potash was added. This made the alkali concentration about 4%. The flask was provided with a return condenser and was heated 6 hours on a steam bath. The alcohol was then distilled off and the product was evaporated to dryness. It was next taken up in a little water, which dissolved almost all of it but a small amount of tar. A benzene or carbon disulfide extraction left the solution entirely clear. To get rid of any dissolved solvent, the solution was warmed. Before acidifying, it was cooled with ice and then was made strongly acid with 20% sulfuric acid. The propiolic acid came down as a brownish oil, which on standing solidified to a porous, brittle solid. This when filtered and dried, did not show itself to be halogen free.

The filtrate was tested with silver nitrate and nitric acid and gave an abundant precipitate of silver bromide, which showed that bromine had been removed in the reaction.

Purification.—The solid was ground up with solid ammonium carbonate and the mixture was treated with a little water. The greater part went into solution and was filtered from a small amount of sticky substance through 3 thicknesses of filter paper. On precipitation, the acid came down as flakes, quite solid. Yield 2.4 g., or 85%. Still, it was not totally halogen-free as indicated by the Beilstein copper-gauze test. One crystallization from carbon tetrachloride, however, gave an acid absolutely halogen-free. M. p., 133–134°. A second recrystallization gave a m. p. of 134–135°. After having been recrystallized from carbon tetrachloride and twice from carbon disulfide the m. p. was 138–139°. However, a portion of the same lot, exposed to air and light, melted at 134–135° with decomposition. 0.062 g. neutralized 2.85 cc. of sodium hydroxide solution (1 cc. = 0.004444 g.) corresponding to a molecular weight of 196.

Properties.—Slightly yellowish white, well-formed microscopic needles from carbon tetrachloride in which it is very soluble hot and only sparingly soluble cold. It is very soluble in carbon disulfide.

Oxidation with Potassium Permanganate.—The following test was performed to distinguish this acid from the acrylic acid. Dil. potassium permanganate solution was immediately decolorized when added to a cold sodium carbonate solution of the pure propiolic acid. This shows it to be unsaturated. An excess of permanganate was added and the tube was heated. No odor of aldehyde could be detected whatsoever, nor did an ether extraction remove anything from the solution. The propiolic acid showed itself to differ in this respect as well as in its melting point from the acrylic acid.

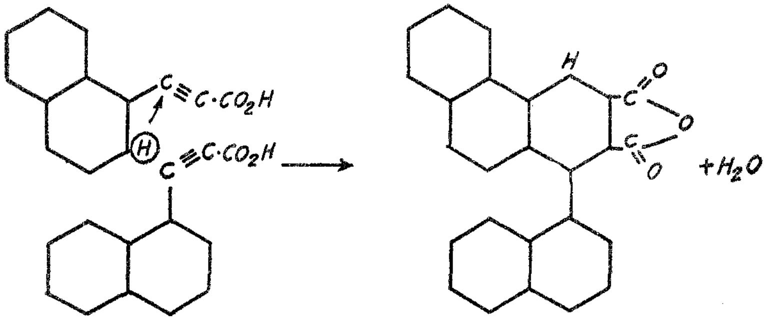
Action of Acetic Anhydride on the Propiolic Acid.

One-half g. of the propiolic acid was heated with 2 cc. of acetic anhydride and immediately went into solution. It was boiled on a return condenser for 5 hours. The solution was then evaporated to $^1/_2$ its volume by distilling off the acetic anhydride under diminished pressure. On cooling, the whole solidified to burr-shaped clusters of needles which, when pressed out on a porous plate and washed with glacial acetic acid, were pure white and melted at 207–209°. This compound showed itself to be saturated in that it would not reduce potassium permanganate in cold solution.

Sodium Salt of the Condensation Product.—Attempts to dissolve this product in sodium hydroxide were attended with great difficulties. Even long boiling failed to have any appreciably noticeable effect on it. The adding of a few drops of 95% alcohol served 2 purposes: it first dissolved a small amount of the compound so that it could come into more intimate contact with the alkali; then too, it helped completely to salt out the sodium salt which appeared as a white solid.

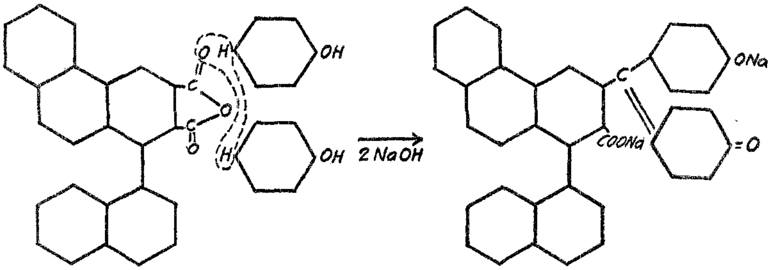
This sodium salt differed widely from any that had been met with in the whole series. First, it was exceedingly insoluble; and then after being dissolved after long boiling in water, it would not reduce potassium permanganate in cold solution.

From the theory already advanced, it is to be supposed that a condensation had taken place analogous to that of the phenyl-propiolic acid series, and that 2 molecules of α-naphthyl-propiolic acid had condensed to form an 8-α-naphthyl-phenanthrene-6,7-dicarboxylic anhydride as follows.



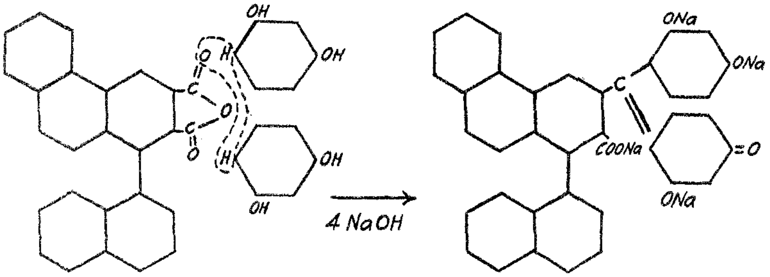
Proof of the Di-ortho Anhydride Condition.

1. **Baeyer's Phthalein Reaction.**—When a few crystals of the condensation product were heated with phenol and a few drops of conc. sulfuric acid, the resulting product was an indicator—red in alkaline solution and colorless in acid solution.



2. **Baeyer's Fluorescein Test.**—A small amount of the condensation product was heated with resorcinol and sulfuric acid for a few minutes. The product, on being poured on water made alkaline with sodium hy-

droxide, showed a very deep, reddish-green fluorescence. The reaction was in all probability as follows.



From all these tests and the extensive work of Michael and Bucher, it seems reasonable to suppose that the new product is 8-α-naphthyl-6,7-phenanthrene-dicarboxylic anhydride.

Summary.

I. It has been shown that α-naphthyl-propiolic acid can be prepared efficiently, satisfactorily, without great expense and in good yields, from commercial naphthalene as a starting point.

II. Incidentally, a satisfactory method has been found for obtaining α-naphthaldehyde, which has long been a most difficult compound to prepare.

III. It is of further interest that the treatment of saturated α,β-dibromo-naphthyl propionic ester with alcoholic potash readily removes both molecules of hydrogen bromide to form the propiolic acid, which is obtained halogen-free with very good yields by the use of ammonium carbonate. In the case of the analogous preparation of phenyl-propiolic acid, it is exceedingly difficult to remove the second molecule of hydrogen bromide.

IV. Finally, it has been shown that the action of acetic anhydride on α-naphthyl-propiolic acid produces a new compound that is saturated and has properties entirely different from the propiolic acid, and that the polymerization has probably produced an 8-α-naphthyl-6,7-phenanthrene-dicarboxylic anhydride.

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