VI. $C_{10}H_7COCH_2CH_2COOH$.—(a) To a mixture of 200 cc. of anhydrous acetylene tetrachloride and 82 g. (0.5 mole) of β-carbethoxypropionyl chloride cooled to 0°, there was added 133 g. (1 mole) of granular anhydrous aluminum chloride. Keeping the temperature at 0°, 64 g. (0.5 mole) of naphthalene in 200 cc. of anhydrous acetylenetetrachloride was added dropwise. The resulting mixture was stirred for three to four hours at 0° and then allowed to come slowly to room temperature overnight. The reaction mixture was decomposed, the solvent and excess naphthalene steam distilled off and the residue extracted twice with ether. The ether extracts were evaporated and the crude ester saponified with 300 cc. of 10% alcoholic sodium hydroxide. The clear alcoholic solution was diluted with water, the alcohol removed *in vacuo*, and, after cooling, the aqueous solution was acidified; yield, 97 g. (85%), m. p. 151.5–156.5°. The crude product was recrystallized from 1,000 cc. of 50% alcohol and allowed to cool slowly at room temperature. The first crop yielded 63 g. (55%) of β-(2-naphthoyl)-propionic acid, m. p. 172.5–173°; literature, 171–173°,[19] 174°.[31] The filtrate on dilution with water yielded 28 g. (25%) of the β-(1-naphthoyl)-propionic acid which melted after recrystallization from dilute acetic acid and aqueous methanol at 129–130°; literature, 129–131°,[19] 131°.[31]

(b) The above described experiment was repeated substituting an equal volume of nitrobenzene for the acetylene tetrachloride. The crude β-(1-naphthoyl)-propionic acid was obtained in a yield of 85 g. (75%), melting at 120–122.5°; recrystallized from dilute acetic acid followed by recrystallization from aqueous methyl alcohol, m. p. 130–131°; mixed m. p. with product obtained under (a), 130–131°.

Summary

1. ω-Aroyl aliphatic acids have been obtained in excellent yield by the Friedel–Crafts reaction of ester-acid chlorides of aliphatic dicarboxylic acids with aryl nuclei.

2. The reaction has been shown to be applicable to benzene, its alkyl, alkoxy and alkyl-alkoxy derivatives as well as to thiophene and to naphthalene.

3. The ω-aroyl aliphatic acids have been reduced to the ω-aryl fatty acids by the Clemmensen method. Reduction with Raney alloy and aqueous alkali and the Wolff–Kishner method were applied in a few cases.

4. Several new ω-aroyl and ω-aryl aliphatic acids are described.

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[31] Schroeter, Muller and Huang, *Ber.*, **62**, 645 (1929).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF SCHERING CORPORATION]

α-Aryloxy and α-Aryl Thiol Cinnamic Acids

BY DOMENICK PAPA AND ERWIN SCHWENK

For studies on the hydrogenolysis of oxygen and thio ethers with Raney alloy and aqueous alkali,[1] several α-phenoxycinnamic acids and α-phenylmercaptocinnamic acids, as well as the corresponding hydrogenated derivatives, were required. The Perkin condensation of sodium phenoxyacetate and benzaldehyde[2] has been described long ago as a convenient preparative method for α-phenoxycinnamic acid and its halogen, alkyl, alkoxy and alkyl–alkoxy derivatives.[3] The corresponding α-phenylmercaptocinnamic acids, however, are not known.[4]

The Perkin condensation of *p*-hydroxybenzaldehyde and either anhydrous sodium or potassium phenoxyacetate yielded the α-phenoxy-*p*-hydroxycinnamic acid. Under similar conditions, benzaldehyde and *p*-hydroxybenzaldehyde and the alkali metal salts of phenyl thioglycolic acid gave the α-phenylmercaptocinnamic acid and α-phenylmercapto-*p*-hydroxycinnamic acid, respectively. Although the yields in these reactions were not entirely satisfactory, the accessibility of the starting materials and the simplicity of the procedure renders the method a useful synthetic tool for the preparation of these compounds.

In a previous publication,[5] it has been shown that cycloalkyl and cycloalkylidene acetic acids may be condensed with aromatic aldehydes in the presence of equimolecular amounts of metallic salts or organic amines. This modification of the Perkin reaction has been found applicable to aryloxy acetic acids as well as to the corresponding thio compounds. The yields of cinnamic acids obtained with either triethylamine or anhydrous potassium acetate are somewhat better than those obtained with the alkali metal salts.[6]

Reduction of the α-phenoxy-*p*-hydroxycinnamic acid and the α-phenylmercapto-*p*-hydroxycinnamic acid to the corresponding propionic acid derivatives was achieved in good yield by sodium amalgam in very dilute alkaline solution.

Experimental

1. α-Phenoxy-*p*-hydroxycinnamic Acid, A.—A mixture of 38 g. (0.25 mole) of phenoxyacetic acid, 30.5 g. (0.25 mole) of *p*-hydroxybenzaldehyde, 25 g. (0.25 mole) of triethylamine and 75 g. of acetic anhydride was heated with stirring at 105–110° for thirty-five to forty hours. The reaction mixture was cooled to 60°, the excess acetic anhydride cautiously decomposed with water, and then poured on ice. The semi-solid residue was extracted with

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[1] A preliminary report of the hydrogenolysis of oxygen and thio ethers with Raney alloy and aqueous alkali was presented before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society on September 11, 1944.

[2] Oglialoro, *Gazz. chim. ital.*, **10**, 483 (1880).

[3] Oglialoro, *ibid.*, **20**, 505 (1890); Stoermer and Biesenbach, *Ber.*, **38**, 1966 (1905).

[4] β-Phenyl mercaptocinnamic acids, however, are readily accessible by the condensation of ethyl phenylpropiolate with sodium thiophenolate, Ruhemann and Stapleton, *J. Chem. Soc.*, **77**, 1181 (1900). The corresponding oxygen analogs are similarly prepared with sodium phenolate, Ruhemann and Beddow, *ibid.*, **77**, 985 (1900).

[5] Schwenk and Papa, THIS JOURNAL, **67**, 1432 (1945).

[6] Compare "Organic Reactions," Vol. I, John Wiley & Sons, Inc., 1942, p. 238-240.

ether, the ether extract washed with water, and then extracted with three 250-cc. portions of 5% sodium carbonate solution. The combined sodium carbonate extracts were neutralized with hydrochloric acid, heated to 70–80°, treated with charcoal, filtered and acidified. The crude α-phenoxy-*p*-hydroxycinnamic acid was obtained in a yield of 26 g. (40%) melting at 236–240°. Recrystallized for analysis from aqueous methyl alcohol, m. p. 245–246°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.70. Found: C, 70.26; H, 4.43.

B. A mixture of 48 g. of anhydrous potassium α-phenoxyacetate, 33 g. of *p*-hydroxybenzaldehyde and 100 cc. of acetic anhydride was heated for ten hours at 150°.[7] The reaction mixture was worked up as described under (A) and there was obtained 19 g. (30%) of the crude cinnamic acid melting at 224–229°. Recrystallized from dilute methyl alcohol, giving 13.4 g., m. p. 240–242°.

II. **α-Phenylmercapto-*p*-hydroxycinnamic Acid. A.**—This compound was prepared as described for the corresponding oxygen analog using 16.8 g. (0.1 mole) of phenylthioglycolic acid, 12.2 g. (0.1 mole) of *p*-hydroxybenzaldehyde, 10 g. (0.1 mole) of triethylamine and 100 cc. of acetic anhydride. The crude α-phenylmercapto-*p*-hydroxycinnamic acid was obtained in a yield of 10 g. (37%) melting at 206–209°. An analytical sample was recrystallized from acetone and water, m. p 211.5–213.5°.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.15; H, 4.45. Found: C, 66.50; H, 4.39.

B. Condensed for thirty-six hours at 100–110°, 51.5 g. (0.25 mole) of anhydrous potassium α-phenylthioglycolate, 30.5 g. (0.25 mole) of *p*-hydroxybenzaldehyde, and 200 cc. of acetic anhydride. The reaction product was worked up as described under I(A), crude yield 42 g. (61%), m. p. 202–206°. Recrystallization from acetone and water gave a product melting at 209–211°.

III. **α-Phenoxy-β-(*p*-hydroxyphenyl)-propionic Acid.**–To a solution of 40 g. of α-phenoxy-*p*-hydroxycinnamic acid in one liter of 1% sodium hydroxide, there was added in 50-g. portions 400 g. of 5% sodium amalgam. Before each addition of sodium amalgam, the solution was made almost neutral with dilute acetic acid. The aqueous solution was decanted from the mercury, filtered through Supercel and acidified after cooling. The crude reduction product amounted to 31 g. and melted at 165.5–166.5°; recrystallized from aqueous acetone, m. p. 169–170°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.74; H, 5.47. Found: C, 69.54; H, 5.10.

IV. **α-Phenylmercapto-β-(*p*-hydroxyphenyl)-propionic Acid.**—Ten grams of the unsaturated compound II was reduced as described for the oxygen analog. A crude yield of 6 g. was obtained melting at 118–119°; recrystallized from dilute alcohol, m. p. 126–127°.

Anal Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.97; H, 5.27.

V. **α-Phenoxycinnamic Acid.**—A mixture of 95 g. (0.5 mole) of anhydrous potassium phenoxyacetate, 53 g. (0.5 mole) of freshly distilled benzaldehyde and 400 cc. of acetic anhydride was heated with stirring at 105–115° for forty-eight hours. The reaction mixture was then cautiously decomposed with water and the crude α-phenoxycinnamic acid filtered, yield 41 g. (34%), m. p. 150–157°. The substituted cinnamic acid was purified by treatment with hot water which removed 10 g. of cinnamic acid, m. p. and mixed m. p. 129–130°. The pure α-phenoxycinnamic acid was obtained in a yield of 26 g. melting at 183.8–184.5° after recrystallization from aqueous alcohol, literature m. p. 179–180°.[2]

VI. **α-Phenylmercaptocinnamic Acid.**—Forty-eight and five-tenth grams (0.25 mole) of anhydrous sodium phenyl thioglycolate and 26.5 g. (0.25 mole) of benzaldehyde in 100 cc. of acetic anhydride were condensed as described for the corresponding oxygen compound. The crude acid was purified by recrystallization from aqueous alcohol and was obtained in a yield of 22 g. melting at 130–132°. The analytical sample which was also obtained by a recrystallization from aqueous alcohol melted at 143–144°.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72. Found: C, 70.05; H, 5.11.

Acknowledgment.—The authors wish to express their appreciation to Miss Hilda Hankin for her assistance.

Summary

The Perkin condensation of phenoxyacetic acid and phenylthioglycolic acid with benzaldehyde and *p*-hydroxybenzaldehyde is reported. The reaction was carried out with the alkali metal salts as well as with the free acid in the presence of triethylamine.

The hydrogenation of the resulting cinnamic acids to the propionic acids was accomplished with sodium amalgam in dilute aqueous alkali.

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[7] These are the reaction conditions described by Oglialoro. Compare with those of preparation IIB and V.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis and Optical Resolution of 4,5,8-Trimethyl-1-phenanthrylacetic Acid[1]

BY MELVIN S. NEWMAN AND ALLEN S. HUSSEY

In a previous publication[2] it was pointed out that there is considerable interference between the methyl groups in any compound of the 4,5-dimethylphenanthrene type. Since compounds of this type have been prepared previously[2] and the preparation of additional examples is herein described, the question of how the methyl groups are situated in space is of interest. Three possibilities may be considered: (1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings.

In this paper we report on the synthesis of 1,4,5-trimethylphenanthrene, VI, and 4,5,8-trimethyl-1-phenanthrylacetic acid, VIII, and on the resolution of the acid VIII.[3] The first alternative

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[1] Most of the material herein presented is taken from the Ph.D. thesis of A. S. H. at O. S. U., March, 1946. Completing experiments on the resolution were carried out by A. S. H. at Northwestern University and by M. S. N. at O. S. U.

[2] Newman, THIS JOURNAL, **62**, 2295 (1940), note references 14–18.

[3] Newman and Hussey, *ibid.*, **69**, 978 (1947).