benzene–petroleum ether as colorless leaflets, the acid melted at 105.5–106.5°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.5; H, 7.7.

4 - Keto - 6 - ethyl - 1,2,3,4 - tetrahydrophenanthrene (XI).—To 0.3 g. of the aforementioned acid in 3 cc. of benzene was added 0.3 g. of phosphorus pentachloride. After standing for one and one-half hours at room temperature, the mixture was chilled and treated with 0.4 cc. of stannic chloride. After fifteen minutes the complex was hydrolyzed and worked up in the customary manner. The cyclic ketone crystallized from dilute alcohol in clusters of colorless needles; m. p. 50–53°; yield, 0.22 g. (80%). After two more recrystallizations, the cyclic ketone melted at 52.5–53.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 85.4; H, 7.2.

3-Ethyl-5-methylphenanthrene (XII). (a) From 4-Keto-7-ethyl-1,2,3,4-tetrahydrophenanthrene.—The reaction between this ketone and methylmagnesium iodide was carried out in the manner described for the isomer. The liquid hydrocarbon obtained by treatment of the methyl carbinol with palladium–charcoal was converted to the picrate, which crystallized from alcohol in clusters of orange needles; m. p. 112–113.5°. Its trinitrobenzene derivative melted at 127–128°, its trinitrotoluene complex at 78–79.5°. Lewis and Elderfield[3] report 111°, 124–125° and 74–76°, respectively, for the melting points of the picrate, trinitrobenzene complex and trinitrotoluene complex.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.8; H, 7.3. Found: C, 92.8; H, 7.6. Calcd. for $C_{17}H_{16}\cdot C_6H_3N_3O_7$: N, 9.35 Found: N, 9.26.

(b) **From 3-Acetyl-5-methylphenanthrene.**—This ketone was reduced in the manner described for its isomer. The hydrocarbon, after being distilled at 250° at 1.5 mm., gave a picrate (m. p. 113.5–115°) identical with that produced above.

Summary

4-Methylphenanthrene reacts with acetyl chloride in the Friedel–Crafts reaction chiefly in the 1-position and to some extent in the 6-position.

The 1-acetyl-4-methylphenanthrene and 3-acetyl-5-methylphenanthrene were reduced to 1-ethyl-4-methylphenanthrene and 3-ethyl-5-methylphenanthrene, respectively. The syntheses of the latter hydrocarbons are described.

ANN ARBOR, MICHIGAN RECEIVED JUNE 22, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF RICHMOND]

The Kolbe Synthesis with Alkyl-*o*-xenols[1]

BY SIDNEY HARRIS[2] AND J. STANTON PIERCE

Harris and Christiansen[3] have shown that some alkyl-*o*-xenols are powerful germicides. A number of alkyl salicylic acids[4] have shown marked therapeutic, germicidal and fungicidal properties. It was thought desirable to carboxylate several alkyl-*o*-xenols.

The *p*-alkyl-*o*-phenylphenols used in this work were prepared by the general methods used by Auwers and Wittig[5] and Harris and Christiansen.[3] The latter investigators acylated *o*-xenol, carried out the Fries rearrangement on the acyl derivatives, and separated and reduced the *o*- and *p*-acyl-*o*-phenylphenols to the corresponding alkyl derivatives.

We have prepared *p*-ethyl-*o*-phenylphenol, *p*-*n*-propyl-*o*-phenylphenol, and *p*-*n*-hexyl-*o*-phenylphenol and have carboxylated these xenols. Their properties are given in Table I.

Preliminary tests carried out on mice by Dr. H. B. Haag, of the Medical College of Virginia, indicate that 3-phenyl-5-ethylsalicylic acid has about the same acute toxicity as aspirin. A study of the analgesic action of 3-phenyl-5-ethylsalicylic acid and 3-phenyl-5-*n*-propylsalicylic acid is being made by Dr. Haag and will be reported elsewhere.

Experimental

Xenyl Esters.—Acylation of *o*-xenol was carried out with acetyl, propionyl, and *n*-caproyl chlorides. Best yields were obtained when the reaction mixture was distilled, without any preliminary purification, from the Claisen flask in which the reaction took place.

5-Acyl-2-hydroxydiphenyls.—The general directions for the Fries rearrangement given by Harris and Christiansen[3] were followed with *o*-xenyl acetate, *o*-xenyl propionate, and *o*-xenyl *n*-caproate. Yields of the 5-acyl-2-hydroxydiphenyls were increased considerably by increasing the ratio of anhydrous aluminum chloride to xenyl ester from 1.1:1

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(2) Submitted in partial fulfillment of the requirements for the degree of Master of Science in the University of Richmond.

(3) Harris and Christiansen, *J. Amer. Pharm. Assoc.*, **23**, 530–536 (1934).

(4) Walter Kropp, U. S. Patent 1,529,704, March 17, 1925, *C. A.*, **23**, 1217 (1929); F. Hoffman-La Roche and Co., A.-G., Swiss Patents 127,649, 131,520; May 17, 1927, *C. A.* **23**, 5012 (1929); H. A. Bruson and Stein, U. S. Patent 1,998,750, April 23, 1935; H. A. Bruson, U. S. Patent 2,022,185, Nov. 26, 1935.

(5) Auwers and Wittig, *J. prakt. Chem.*, **108**, 99–112 (1924).

TABLE I

	Yield, %	B. p. or m. p. uncor., °C.	Specific density 25/4°	$n^{25}D$	Analyses,[h] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Dilution at which *Staph. aureus* 500,000,000 cc. killed in 5 min.[g]
o-Xenyl acetate[a]	97	139[b]–141$_1$ mm.							
o-Xenyl propionate[c]	97	153–155$_2$ mm.	1.094	1.5641					
o-Xenyl *n*-caproate	96	174–177$_{1.5}$ mm.	1.043	1.5447	80.55	79.94	7.52	7.80	
5-Acetyl-2-[a]hydroxydiphenyl	62[d]	167–168.5							
5-Propionyl-2-[c]hydroxydiphenyl	46	147.5–148							
5-*n*-Caproyl-2-hydroxydiphenyl	47	86– 88			80.55	80.52	7.52	7.87	
5-Ethyl-2-[a,c]hydroxydiphenyl	70	141–143$_1$ mm.							1—13,000
5-*n*-Propyl-2-hydroxydiphenyl	74	150–152$_{0.9}$ mm.							1—25,000
5-*n*-Hexyl-2-hydroxydiphenyl	60	190–194$_2$ mm.	1.024	1.5697	84.98	83.95	8.72	8.97	1—25,000
3-Phenyl-5-ethylsalicylic acid[e]	55	161–164			74.35	73.87	5.83	6.18	1— 1,750
3-Phenyl-5-*n*-propylsalicylic acid[f]	49	137–143.5			74.96	74.11	6.30	6.61	1— 750
3-Phenyl-5-*n*-hexylsalicylic acid	9	131–134			76.46	76.07	7.44	7.66	1— 1,750
Acetyl-3-phenyl-5-ethylsalicylic acid	73	156–160.5			71.80	70.97	5.68	6.14	
Acetyl-3-phenyl-5-*n*-propylsalicylic acid	69	148–151			72.45	71.78	6.09	6.43	

[a] Prepared by Auwers and Wittig.[5] [b] M. p. of *o*-xenyl acetate 63–63.5°. [c] Prepared by Harris and Christiansen.[3] [d] Yields of 5-acyl-2-hydroxydiphenyls reported are after one recrystallization. The melting points for these compounds as tabulated are 164–168°, 142–147.5°, and 84–87.5°. [e] Neutral equivalent of 3-phenyl-5-ethylsalicylic acid: calcd., 242.1; found 242.3. [f] Neutral equivalent of 3-phenyl-5-*n*-propylsalicylic acid: calcd., 256.1; found 258.2. [g] Bacteriological tests were carried out by Mr. W. L. Williams, University of Louisville School of Medicine.

Harris and Christiansen,[3] in the study of bactericidal properties of 5-alkyl-2-hydroxydiphenyls, used an aqueous–alcohol–glycerol solvent, containing 25 and 35% by volume of alcohol and glycerol, respectively. Not all of the germicides tested above were held in solution by the above solvent, so the amount of alcohol was doubled, yielding 40.0 and 28.0% by volume of alcohol and glycerol, respectively. Each solution contained 0.2% of germicide, initially. These solutions were added to 0.5 cc. of culture (500,000,000 per cc.) to give the dilution of germicide indicated. After an exposure of five minutes, subcultures were made and incubated for forty-eight hours.

[h] Microanalyses were made by Dr. Johannes Hoppe, of Munich, Germany.

to about 1.5:1, or higher. In each case the crude reaction product, after being heated, was powdered, added to ice and 5% hydrochloric acid, and warmed to dissolve aluminum salts. Then the mixture was cooled, ice and solid sodium hydroxide were added with stirring and the strongly basic mixture was filtered. The acylxenol was obtained from the filtrate by acidification with concentrated hydrochloric acid and suction filtration. Partial purification was effected by washing with water, drying on a porous plate or paper towel, and extracting with warm petroleum ether (b. p. 35–60°). The residue, which consisted largely of 5-acyl-2-hydroxydiphenyl, was purified by recrystallization. Alcohol and water, benzene and ligroin, ligroin and alcohol, ligroin, and a mixture of benzene, ligroin, and alcohol were used in various crystallizations.

The petroleum ether extracts, on evaporation, yielded oils or gummy solids. These gave dark colors when aqueous alcohol solutions were treated with ferric chloride as did the 3-acyl-2-hydroxydiphenyls prepared by Harris and Christiansen.[3] This test was not obtained with pure 5-acyl-2-hydroxydiphenyls. All these facts indicate that the oily or gummy residues obtained on evaporation of the petroleum ether extracts were crude 3-acyl-2-hydroxydiphenyls. The percentage yields of crude products from petroleum ether were 3.3, 3.4 and 6.6%, respectively, for the 3-acetyl, 3-propionyl, and 3-*n*-caproyl compounds.

***p*-Alkyl-*o*-phenylphenols.**—The reduction of 5-acyl-2-hydroxydiphenyls was carried out by the method of Clemmensen, as modified by Harris and Christiansen[3] for this series of compounds. These investigators reported some pinacol formation, yet obtained excellent yields of *p*-alkyl-*o*-phenylphenols. In this Laboratory, poor yields were obtained in most runs when the mixture was briskly agitated, as recommended by Harris and Christiansen. Best results were obtained by the addition of acetic acid and by gentle refluxing from twenty-four to forty-eight

hours. In some runs, following the method of Martin,[6] the addition of toluene and acetic acid gave excellent results.

3-Phenyl-5-alkylsalicylic Acids.—The method described by Vorozhtsov and Troshchenko[7] for the carboxylation of *o*-phenylphenol was used for the introduction of carbon dioxide into *p*-alkyl-*o*-phenylphenols. The preparation of a typical 3-phenyl-5-alkylsalicylic acid is described.

An intimate mixture of 14 g. of *p*-propyl-*o*-phenylphenol and 95 g. of finely powdered anhydrous potassium carbonate was introduced into a steel tube of 180 ml. capacity and 18 g. of dry-ice was added. The tube was heated at 110° for one hour and the temperature was raised 10° per hour until 200° was reached. After one hour the temperature was raised to 225° and maintained for fourteen hours. The tube was cooled and the contents were poured into a beaker. Two hundred ml. of water was added and the mixture was acidified with concentrated hydrochloric acid. The oil which first formed solidified to a gummy solid. The precipitate was filtered and recrystallized once from acetic acid and water. The yield was 8.29 g. or 49% of theoretical, melting 127–136°. On further purification the product melted 137–143.5°.

3-Phenyl-5-ethylsalicylic acid was prepared similarly in excellent yield. However, by the same general method only a very low yield of 3-phenyl-5-*n*-hexylsalicylic acid was obtained. This low yield may be due to the high molecular weight and corresponding insolubility of the potassium salt of *p*-hexyl-*o*-phenylphenol or, as Harris and Christiansen[3] suggest, to the diminution of the acidic character of the phenol as the alkyl group increases in size.

The 3-phenyl-5-alkylsalicylic acids prepared were practically insoluble in water but were quite soluble in alcohol, benzene, ether, and glacial acetic acid. All dissolved in dilute alkali.

Acetyl-3-phenyl-5-alkylsalicylic Acids.—3-Phenyl-5-ethylsalicylic acid and 3-phenyl-5-*n*-propylsalicylic acids were acetylated with acetyl chloride and acetic acid. The excess acetyl chloride and most of the acetic acid were removed by evaporation below 75°, finally in partial vacuum. For purification, the acetyl derivatives were dissolved in absolute alcohol and precipitated by the addition of ice and ice water. This procedure would not remove unacetylated 3-phenyl-5-alkylsalicylic acid or this product formed on hydrolysis of the acetylated derivative, so the melting points reported likely are slightly in error. The above acetyl-3-phenyl-5-alkylsalicylic acids are insoluble in water. They dissolve readily in ether, alcohol, benzene, and dilute alkali.

(6) Elmore L. Martin, THIS JOURNAL, **58**, 1438 (1936).

(7) Vorozhtsov and Troshchenko, *C. A.*, **32**, 7907 (1938); *J. Gen. Chem.* (U. S. S. R.), **8**, 424–429 (in English, 430) (1938).

Summary

3-Phenyl-5-ethylsalicylic acid, 3-phenyl-5-*n*-propylsalicylic acid, and 3-phenyl-5-*n*-hexylsalicylic acid were made by the carboxylation of *p*-ethyl-, *p*-*n*-propyl-, and *p*-*n*-hexyl-*o*-phenylphenol, respectively.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Absorption Studies of Some Hydrocarbons

BY F. T. WALL AND G. W. MCMILLAN

Spectroscopic studies of various hydrocarbons have shown that the valence vibrations associated with C–H bonds have absorption wave lengths in the neighborhood of 3.3 μ. Considerable variation in the wave lengths is observed, however, although one important general effect was noticed by Bonino.[1a] He pointed out that the wave lengths for aromatic C–H bonds were usually lower than those for the aliphatic type. The same effect was observed by Buswell, Rodebush and Roy.[1b] This experimental generalization suggests that one could use absorption frequencies as a spectroscopic criterion for aromatic character.

For example, infrared absorption studies of the phenylmethanes demonstrated clearly the presence or absence of aliphatic and aromatic hydrogens. It was found[2] that molecules such as benzene and tetraphenylmethane, which have only aromatic hydrogens, showed absorption peaks in the neighborhood of 3.25 μ which could be attributed to aromatic carbon–hydrogen bond vibrations. It also was found that toluene, di- and triphenylmethanes[2,3] likewise showed absorption in the 3.25 μ region which could be assigned to their aromatic hydrogens. In addition, however, the latter molecules showed absorption in the neighborhood of 3.45 μ which was absent in the case of benzene and tetraphenylmethane. Accordingly the peaks in the 3.45 μ region were attributed to modes of vibration involving for the most part aliphatic carbon–hydrogen bonds.

The phenylmethane series provided a relatively

(1) (a) G. B. Bonino, *Trans. Faraday Soc.*, General Discussion, 879 (1929); (b) Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2444 (1938).

(2) F. T. Wall and G. W. McMillan, *ibid.*, **61**, 1053 (1939).

(3) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A167**, 257 (1938).