5-Indanol (II) was also isolated by Dr. Woolfolk from coal-hydrogenation oils. It had a melting point of 52.4–53.8°.

5-Hydroxy-1,2,3,4-tetrahydronaphthalene (III) was prepared from pure 1-naphthol by hydrogenation.[6] Repeated crystallization gave a spectroscopically pure sample, m. p. 67.8–69.0°.

6-Hydroxy-1,2,3,4-tetrahydronaphthalene (IV) was prepared by the hydrogenation of 2-naphthol according to the directions of Stork.[7] We experienced considerable difficulty in freeing the tetrahydro compound from its aromatic precursor. Purification was achieved by distributing the mixture between cyclohexane and an aqueous alkaline buffered (*p*H 12.5) solution. In such a system all the 2-naphthol and a portion of the tetrahydronaphthol is retained in the aqueous phase and the organic phase contains pure tetrahydronaphthol. The tetrahydro compound was recovered from the organic phase by distillation and recrystallization. The pure material had a melting point of 57.2–58.4° and its ultraviolet absorption spectrum indicated the absence of naphthol.

Partition Experiments.—The phenols were dissolved in 20 ml. of spectrographic grade cyclohexane (0.5 mg. per ml.) and shaken with an equal volume of water for two minutes. After phase separation, the concentration of the phenol in the organic phase was determined by ultraviolet spectrophotometry in the usual way.[4]

(6) Musser and Adkins, THIS JOURNAL, **60**, 664 (1938).

(7) Stork, *ibid.*, **69**, 576 (1947).

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The Reaction of Sodium Hypobromite with Arylcyanopyruvic Esters

BY SIGVARD WIDEQVIST

The appearance of a paper on the bromination of esters of arylcyanopyruvic acid[1] has prompted us to report some experiments, carried out some years ago, on the reaction between sodium hypobromite and certain organic compounds having labile hydrogen atoms. One of these was ethyl phenylcyanopyruvate. It was found that a cleavage of the ester took place with the production of phenylbromoacetonitrile, probably according to the equation

$$C_6H_5—CH(CN)—COCOOC_2H_5 + NaOBr \longrightarrow C_6H_5—CH(CN)Br + NaOCOCOOC_2H_5$$

This reaction was later used for synthetic purposes.

Treatment of an alkaline solution of ethyl phenylcyanopyruvate with an iodine–potassium iodide solution yielded a crystalline iodo compound, presumably phenyliodoacetonitrile, which, however, was very unstable and decomposed with the liberation of iodine. Ethyl α-naphthylcyanopyruvate was also cleaved in the same manner.

Phenylbromoacetonitrile.—Twenty-one and seven-tenths grams (0.1 mole) of ethyl phenylcyanopyruvate was dissolved in 200 cc. of water containing 5 g. of sodium hydroxide. The solution was cooled to 0°, and an ice-cold mixture of 16 g. of bromine, 9 g. of sodium hydroxide and 100 cc. of water was added. Phenylbromoacetonitrile immediately separated as a heavy, lemon-yellow oil; yield 16 g. (82%). It was converted into diphenylacetonitrile by the Friedel–Crafts reaction.

α-Naphthylbromoacetonitrile.—Ethyl α-naphthylcyanopyruvate (m. p. 114–115°, prepared from α-naphthylacetonitrile and diethyl oxalate; yield 73%) 5.0 g. (0.019 mole) was dissolved in 35 cc. of 2 *N* sodium hydroxide solution and cooled to 0°. A cold mixture of 5 g. of bromine and 40 cc. of 2 *N* sodium hydroxide was added. α-Naphthylbromoacetonitrile immediately separated as an orange-yellow oil which solidified in a few minutes; yield 4 g. (87%). It was recrystallized from hot alcohol (m. p. 101–102°).

Anal. Calcd for $C_{12}H_8NBr$: C, 58.54; H, 3.28; N, 5.69; Br, 32.49. Found: C, 58.80; H, 3.42; N, 5.59; Br, 32.92.

(1) Skinner, Kleibacker, Rosenberg, Gladner and Reed, THIS JOURNAL, **70**, 4011 (1948).

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The Synthesis of 2-Fluoro-4- and 2-Fluoro-6-pyridinecarboxylic Acid and Derivatives

BY ARTHUR ROE, P. H. CHEEK AND G. F. HAWKINS[1]

The synthesis of 2-fluoronicotinamide,[2] 5-fluoronicotinamide[3] and 6-fluoronicotinamide[2] has been reported; preliminary reports indicate that at least one of them acts as a growth inhibitor for some microörganisms. It was therefore of interest to prepare some fluorinated isomers of nicotinic acid; this note reports the preparation of 2-fluoro-4-pyridinecarboxylic acid and 2-fluoro-6-pyridinecarboxylic acid together with their methyl esters and amides. The synthesis involved preparation of 2-fluoro-4-methylpyridine and 2-fluoro-6-methylpyridine followed by oxidation to the fluoro acids.

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Experimental

The preparation of the fluoromethylpyridines and fluoro acids was carried out as described[2,3] for the fluoronicotinic acids, except that the water solubility of the 2-fluoro-6-pyridinecarboxylic acid made it necessary to remove the water from the acidified oxidation concentrate; this was accomplished by addition of ethanol and benzene, with subsequent distillation, in a manner somewhat similar to that reported by Black, Depp and Corson.[4] The acid was extracted from the inorganic material with benzene–alcohol. The methyl esters were obtained by allowing the acids to react with diazomethane[3]; the amides were prepared by the reaction of the methyl esters with 1:1 methanol–liquid ammonia mixture. The properties and analyses of the compounds prepared are given in Table I.

(1) Present address: Tennessee Eastman Corporation, Kingsport, Tennessee.

(2) Minor, Hawkins, VanderWerf and Roe, THIS JOURNAL, **71**, 1125 (1949).

(3) Hawkins and Roe, *J. Org. Chem.*, **14**, 328 (1949).

(4) Black, Depp and Corson, *ibid.*, **14**, 14 (1949).