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]

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[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.

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

CHEMICAL INSTITUTE
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UPPSALA, SWEDEN
RECEIVED JULY 11, 1949

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.

The authors are indebted to Eli Lilly and Company for generous support of this and related projects.

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.

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[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).

TABLE I

Compound	M. p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Found
2-Fluoro-4-methylpyridine	[a]	36	C_6H_6NF	12.6	12.8
2-Fluoro-6-methylpyridine	[b]	34	C_6H_6NF	12.6	12.8
2-Fluoro-4-pyridinecarboxylic acid	195–197[c]	34	$C_6H_4O_2NF$	9.93	9.69, 9.88
2-Fluoro-6-pyridinecarboxylic acid	135–137	50	$C_6H_4O_2NF$	9.93	9.77, 9.86
Methyl 2-fluoro-4-pyridinecarboxylate	[d]	84	$C_7H_6O_2NF$	9.03	8.93
Methyl 2-fluoro-6-pyridinecarboxylate	53-54.5	76	$C_7H_6O_2NF$	9.03	9.05
2-Fluoro-4-pyridinecarboxamide	173–174	100	$C_6H_5ON_2F$	20.00	20.14
2-Fluoro-6-pyridinecarboxamide	134–135	100	$C_6H_5ON_2F$	20.00	19.83, 19.81

[a] Liquid, b. p. 157°; $n^{25}D$ 1.4690; $d^{25}{}_4$ 1.0805. [b] Liquid, b. p. 142°; $n^{25}D$ 1.4673; $d^{25}{}_4$ 1.0762. [c] Taken in the usual manner, the material contracted sharply at 188°, but no definite transition to the liquid state was observed upon further heating. If the bath were pre-heated to 195–197° the material when inserted melted quickly to a liquid, but re-solidified at once. [d] Liquid, b. p. 91° at 13 mm.; $n^{25}D$ 1.4843.

DEPARTMENT OF CHEMISTRY
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CHAPEL HILL, N. C.

RECEIVED JUNE 11, 1949

Some Cyclic Acetals of Tris-(hydroxymethyl)-nitromethane and their Derivatives

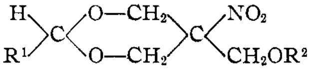
BY ALLEN SCATTERGOOD AND ALAN L. MACLEAN[1]

The cyclic acetals derived from tris-(hydroxymethyl)-nitromethane and five different aldehydes have been reported by Senkus[2] who prepared them by the azeotropic removal of water from equimolar quantities of the nitro triol and the aldehyde in the presence of a catalytic amount of *p*-toluenesulfonic acid. These cyclic acetals are the 5-nitro-5-(hydroxymethyl)-2-alkyl-1,3-dioxanes and should theoretically be capable of existing in both *cis* and *trans* forms. Although *cis–trans* isomers of cyclic acetals of tris-(hydroxymethyl)-nitromethane have never been obtained, Senkus[3] has prepared two sets of *cis–trans* isomers of cyclic acetals of a nitro glycol.

It seemed possible that tris-(hydroxymethyl)-nitromethane might serve as a model polyol useful in exploring conditions that could be employed in the acid catalyzed formation of cyclic acetals of carbohydrates or their derivatives in aqueous solution. Accordingly this triol was allowed to react with several aldehydes in an aqueous medium that was two molar in both reactants and also in hydrochloric acid. Three of the aldehydes formed crystalline acetals under these conditions. Two of these crystalline acetals were derived from aldehydes previously employed by Senkus. However, these acetals melted at higher temperatures than the acetals obtained by Senkus. It is probable that the compounds isolated by Senkus are *cis–trans* isomers of the ones prepared by us. We have demonstrated the presence of a free hydroxyl group in all of our acetals by the formation of their crystalline benzoates. We have also secured one *p*-toluenesulfonate and a cyanoethylation product. The properties of the new compounds are given in Table I.

TABLE I

SOME ACETALS OF THE TYPE



R^1	R^2	Yield, %	Solvent	M. p. (cor.), °C.	Empirical formula	Calculated, % C	H	N	Analyzed, %[c] C	H	N
C_6H_5	H	74	Ethanol–water	124.8	$C_{11}H_{13}O_5N$	55.2	5.44	5.85	55.19	5.48	6.04
C_6H_5	C_6H_5CO	90	Isobutyl alcohol	116.2	$C_{18}H_{17}O_6N$	63.1	4.96	4.08	63.11	4.96	4.25
C_6H_5	$SO_2C_6H_4CH_3$	90	Isobutyl alcohol	143.3	$C_{18}H_{19}O_7NS$	54.9	4.83	3.56	54.61	4.96	3.68[d]
n-C_3H_7	H	81	*n*-Hexane	100.2[a]	$C_8H_{15}O_5N$	46.8	7.31	6.82	46.93	7.47	6.83
n-C_3H_7	C_6H_5CO	..	Isobutyl alcohol	107.0	$C_{15}H_{19}O_6N$	58.2	6.15	4.53	57.94	6.14	4.59
$(C_2H_5)_2CH$	H	65	*n*-Hexane	81.2[b]	$C_{10}H_{19}O_5N$	51.5	8.15	6.01	51.5	8.21	6.28
$(C_2H_5)_2CH$	C_6H_5CO	..	*n*-Hexane	63.1	$C_{17}H_{23}O_6N$	60.5	6.82	4.15	60.40	6.88	4.26
C_6H_5	CH_2CH_2CN	..	*n*-Hexane	77.7	$C_{14}H_{16}O_5N_2$	57.5	5.48	9.6	58.5	5.47	9.60

[a] Senkus[2] reported a melting point of 69.8° for the acetal prepared by his method. [b] Senkus[2] reported a melting point of 70.3° for the acetal prepared by his method. [c] The microanalyses were performed by Mr. S. M. Nagy and Mrs. Louise W. Spencer. [d] Calcd. for $C_{18}H_{19}O_7NS$: S, 8.14. Found: S, 8.19.

Experimental

Cyclic Acetals of Tris-(hydroxymethyl)-nitromethane.—One-tenth mole (15.1 g.) of tris-(hydroxymethyl)-nitromethane (supplied by the Commercial Solvents Corporation, Terre Haute, Indiana), 10 cc. of water, 8 cc. (0.1 mole) of concentrated hydrochloric acid and 10 cc. of methyl cellosolve (to act as a mutual solvent, omitted in the case of *n*-butyraldehyde) and 0.1 mole of the aldehyde were mixed, and the volume of the mixture (which may be two phase) was made up to 50 ml. with water. Thus the mixture was two molar in each of the reactants and also in hydrochloric acid. Homogeneous mixtures were allowed

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[1] The material in this note is taken in part from a thesis submitted to the Massachusetts Institute of Technology by Alan L. MacLean in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

[2] Senkus, THIS JOURNAL, **63**, 2635 (1941).

[3] Senkus, *ibid.*, **65**, 1658 (1943).