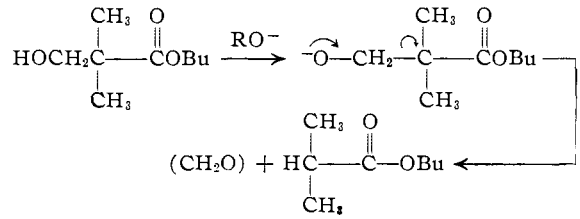
TABLE I

PHYSICAL CONSTANTS AND DERIVATIVES OF ALCOHOLS, ALDEHYDES AND KETONES ISOLATED

Compound	B.p., °C. Obsd.	B.p., °C. Reptd.[a]	Derivative prepared	M.p. deriv., °C. Obsd.	M.p. deriv., °C. Reptd.[a]
Methanol	63–65	64.6	3,5-DNB[b]	107–108	107.5
Isobutyraldehyde	63–65	64	2,4-DNPH[c]	186–187	187
Isobutyl alcohol	106–108	108	3,5-DNB	86–87	87
2-Ethylbutyraldehyde	115–118	117	2,4-DNPH	92–94	94.5–95
2-Ethyl-1-butanol	146–149	149.5	3,5-DNB	50–51	51.5
2-Methylvaleraldehyde	114–118	116	2,4-DNPH	102–104	103
2-Methyl-1-pentanol	145–149	148	3,5-DNB	49–50	50.5
2,4-Dimethyl-3-pentanone	123–125	124	2,4-DNPH	85–86	85–86

[a] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds. Order I," John Wiley and Sons, Inc., New York, N. Y., 1941. [b] 3,5-Dinitrobenzoate. [c] 2,4-Dinitrophenylhydrazone.

went primarily an ester-interchange leading to the formation of a polyester, but small amounts of methanol, carbon monoxide and butyl isobutyrate were isolated.



On the other hand, 3-amino-2,2-dimethyl-1-propanol was distilled from dissolved sodium without decomposition.

Experimental

Materials.—The diols are commercially available products which were used without purification. An exception was 2-ethyl-1,3-propanediol, which was prepared by the lithium aluminum hydride reduction of diethyl ethylmalonate. 3-Amino-2,2-dimethyl-1-propanol was prepared as described by Caldwell.[6] We are indebted to Mr. T. E. Stanin, of these laboratories, for a sample of butyl hydroxypivalate.

Analysis of Products.—In all cases the alcohols and aldehydes or ketones produced were well-known compounds which were identified by boiling points and by the preparation of at least one known derivative (see Table I). Analyses of the gaseous products from the reactions invariably showed around 95% to be carbon monoxide and the weights of carbon monoxide produced, which are reported below, are simply the weight losses observed in the reactions.

Cleavage of 2,2-Dimethyl-1,3-propanediol.—2,2-Dimethyl-1,3-propanediol (100 g., 0.96 mole) containing 1 g. of dissolved sodium was heated for 3 hr. at 145–175° while the decomposition products were removed through a 6-inch Vigreux column. From this reaction 8 g. (0.29 mole) of carbon monoxide and 72 g. of distillate were obtained. Fractionation of the distillate gave 10.4 g. (0.14 mole) of isobutyraldehyde and 19.3 g. (0.6 mole) of methanol (part of which was obtained as the methanol–isobutyraldehyde azeotrope, b.p. 59°, which contains about 64% isobutyraldehyde), and 35.9 g. (0.49 mole) of isobutyl alcohol.

Cleavage of 2,2-Diethyl-1,3-propanediol.—Reaction of 99 g. (0.75 mole) of this diol with 1 g. of dissolved sodium under the above conditions gave 10 g. (0.37 mole) of carbon monoxide and 60 g. of distillate. Fractional distillation gave 12 g. (0.38 mole) of methanol, from 1 to 2 g. of 2-ethylbutyraldehyde, and 44 g. (0.43 mole) of 2-ethyl-1-butanol.

Cleavage of 2-Methyl-2-propyl-1,3-propanediol.—Reaction of 132 g. (1.0 mole) of this diol with 1 g. of dissolved sodium under the above conditions gave 15 g. (0.53 mole) of carbon monoxide and 87 g. of distillate. Fractional distillation gave 17 g. (0.53 mole) of methanol, 6 g. (0.06 mole) of 2-methylvaleraldehyde and 58 g. (0.57 mole) of 2-methyl-1-pentanol.

Cleavage of 2,2,4-Trimethyl-1,3-pentanediol.—Similarly, a mixture of 86.7 g. (0.59 mole) of 2,2,4-trimethyl-1,3-pentanediol and 0.8 g. of dissolved sodium over a 35-minute period at 130–155° gave 0.9 g. (0.03 mole) of carbon monoxide and 74.9 g. of distillate. The distillate on fractionation gave 1.5 g. (0.05 mole) of methanol, 7.8 g. (0.11 mole) of isobutyraldehyde, 45.8 g. (0.62 mole) of isobutyl alcohol, 5 g. (0.04 mole) of 2,4-dimethyl-3-pentanone, and about 4 g. (0.03 mole) of isobutyl isobutyrate, b.p. 145–150°. The isobutyl isobutyrate presumably arose from the Tishchenko reaction of isobutyraldehyde.

Anal. Calcd. for $C_8H_{16}O_2$ (for isobutyl isobutyrate): sapn. equiv., 144.2. Found: sapn. equiv., 146.0.

Cleavage of Butyl Hydroxypivalate.—In a like manner, reaction of 100 g. (0.57 mole) of butyl hydroxypivalate and 1 g. of dissolved sodium over a 30-minute period at 140–185° gave 3 g. (0.11 mole) of carbon monoxide and 35 g. of distillate. From this distillate 3.4 g. (0.11 mole) of methanol, 21 g. (0.28 mole) of butyl alcohol and 3 g. (0.02 mole) of butyl isobutyrate, b.p. 154–155°, $n^{20}D$ 1.4032, were obtained.

Anal. Calcd. for $C_8H_{16}O_2$ (for butyl isobutyrate): sapn. equiv., 144.2. Found: sapn. equiv., 145.0.

Attempted Cleavage of 3-Amino-2,2-dimethyl-1-propanol.—This amino alcohol distilled unchanged at 185–188° (atm. press.) from 1% of its weight of dissolved sodium.

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(6) J. R. Caldwell, U. S. Patent 2,618,658 (1952).

Bromination Products of Nitropyridine

BY ELLIS V. BROWN AND HENRY T. BURKE

RECEIVED JUNE 29, 1955

In the course of an investigation in progress in our laboratories we became interested in the preparation of the various monobromo and dibromo compounds which could be obtained from nitration, diazotization and bromination of 2-aminopyridine and 2-amino-6-methylpyridine.

The nitration procedure of Caldwell and Kornfeld[1] was readily adapted to the nitration of the aminopicoline, by keeping the temperature below 20° during the nitration and below 25° initially in the rearrangement of the intermediate nitroamine. The rearrangement was finally completed by heating the mixture at 40° for one hour. The diazotizations followed the procedure of Baumgarten and Su,[2] although our average yields in 21 runs were 65% for the diazotization of the 2,3-isomer and 71% for the 2,5-isomer. We found that 2-hydroxy-3-nitro-6-methylpyridine melted at 229–230°, and the 2,5-isomer melted at 241–242° when each was recrystallized from water. The starting

(1) W. T. Caldwell and E. C. Kornfeld, THIS JOURNAL, **64**, 1695 (1942).

(2) H. E. Baumgarten and H. C. Su, *ibid.*, **74**, 3828 (1952).

compounds were 2-hydroxy-3-nitro-, 2-hydroxy-5-nitro, 2-hydroxy-3-nitro-6-methyl- and 2-hydroxy-5-nitro-6-methylpyridine.

When 2-hydroxy-3-nitropyridine was treated with molecular bromine and phosphorus tribromide according to the procedure of Berrie, Newbold and Spring,[3] we obtained, in addition to the expected 2-bromo-3-nitropyridine, a small quantity of 2,5-dibromo-3-nitropyridine.

The position of the substituents in the dibromo compound was determined by first treating the 2-hydroxy-3-nitropyridine with molecular bromine to obtain 2-hydroxy-3-nitro-5-bromopyridine which on treatment with phosphorus tribromide gave a dibromo compound identical with the original compound.

The structure of the 2-hydroxy-3-nitro-5-bromopyridine was proved by first brominating 2-aminopyridine using the method of Case,[4] nitrating the resulting 2-amino-5-bromopyridine, and finally diazotizing the resulting 2-amino-3-nitro-5-bromopyridine. Replacement of the hydroxyl group was performed using phosphorus tribromide and phosphorus oxybromide.

Our experiments with 2-hydroxy-3-nitropyridine were extended to other hydroxy compounds. The procedure for the proof of structure was the same as outline above except that when the nitro group was in the five position the original amino compound was first nitrated and then brominated. This sequence was necessary since otherwise bromine entered the five position.

For the bromination and nitration of 2-amino-6-methylpyridine we used the procedure of Adams and Schrecker.[5] For the bromination of 2-amino-5-nitro-6-methylpyridine we followed the procedure of Parker and Shive.[6]

Of the nine possible bromination products which can be obtained from 2-hydroxy-5-nitro-, 2-hydroxy-3-nitro-6-methyl- and 2-hydroxy-5-nitro-6-methylpyridine only two have been reported previously: 2-bromo-5-nitropyridine by Yamamoto,[7] and 2-hydroxy-3-bromo-5-nitro-6-methylpyridine by Parker and Shive.[6]

Acknowledgment.—We are indebted to the Nepera Chemical Co., Inc., for financial aid during this investigation.

Experimental

2-Bromo-3-nitropyridine.—A mixture of 5 g. of 2-hydroxy-3-nitropyridine, 4 ml. of phosphorus tribromide and 0.5 g. of phosphorus oxybromide, was heated on an oil-bath so that the temperature increased to 180° over the course of one hour. It was maintained at that temperature for 0.5 hour, cooled slightly, and the reaction quenched in ice and water. The precipitate was filtered and steam distilled. The distillate was filtered and air-dried to give 4.3 g. (54%) of product, m.p. 123–125°. Berrie, *et al.*,[3] reported 125°.

2-Bromo-5-nitropyridine: colorless needles, m.p. 137–138°, yield 45%. Yamamoto[7] reported 70% yield, m.p. 137° from phosphorus and bromine.

2-Bromo-3-nitro-6-methylpyridine: colorless needles, m.p. 71–72°, yield 24%. *Anal.* Calcd. for $C_6H_5O_2N_2Br_2$: C, 33.19; H, 2.30; Br, 36.85; N, 12.95. Found: C, 33.25; H, 2.39; Br, 36.89; N, 13.1.

2-Bromo-5-nitro-6-methylpyridine: colorless needles, m.p. 69–70°, yield 51%. *Anal.* Calcd. for $C_6H_5O_2N_2Br_2$: C, 33.19; H, 2.30; Br, 36.85; N, 12.95. Found: C, 33.13; H, 2.30; Br, 36.80; N, 13.1.

2,5-Dibromo-3-nitropyridine[8]: colorless needles, m.p. 94–95°, yield 51%. *Anal.* Calcd. for $C_5H_2O_2N_2Br_2$: C, 21.28; H, 0.71; Br, 57.01; N, 9.73. Found: C, 21.35; H, 0.74; Br, 56.93; N, 9.75.

2,3-Dibromo-5-nitropyridine: colorless needles, m.p. 75–76°, yield 90%. *Anal.* Calcd. for $C_5H_2O_2N_2Br_2$: C, 21.28; H, 0.71; Br, 57.01; N, 9.73. Found: C, 21.30; H, 0.76; Br, 57.03; N, 9.83.

2,5-Dibromo-3-nitro-6-methylpyridine: colorless needles, m.p. 87–88°, yield 90%. *Anal.* Calcd. for $C_6H_4O_2N_2Br_2$: C, 24.25; H, 1.35; Br, 54.49; N, 9.46. Found: C, 24.25 H, 1.39; Br, 54.53; N, 9.87.

2,3-Dibromo-5-nitro-6-methylpyridine: colorless needles, m.p. 111–112.5°, yield 66%. *Anal.* Calcd. for $C_6H_4O_2N_2Br_2$: C, 24.25; H, 1.35; Br, 54.49; N, 9.46. Found: C, 23.98; H, 1.39; Br, 54.76; N, 9.91.

2-Hydroxy-3-nitro-5-bromopyridine.—Bromine (1.8 ml.) was slowly added with rapid stirring to 5 g. of 2-hydroxy-3-nitropyridine. The reaction mixture at first became quite warm and when it started to cool it was heated on a steam-bath for two hours. It was then poured on a mixture of ice and water. The oil which separated crystallized overnight and the excess bromine was removed with bisulfite. The solid was filtered and recrystallized from 500 ml. of water using charcoal. The product was obtained in the form of yellow needles, m.p. 245–247°, yield 2.4 g. (33%). The product was also obtained by diazotization of 2-amino-3-nitro-5-bromopyridine using the precedure outlined by Berrie, *et al.*[3]

2-Hydroxy-3-bromo-5-nitropyridine: colorless needles, m.p. 221–223°, yield 85%; also obtained by diazotization of 2-amino-3-bromo-5-nitropyridine.[9] *Anal.* Calcd. for $C_5H_3O_3N_2Br$: C, 27.39; H, 1.37; Br, 36.58; N, 12.29. Found: C, 27.41; H, 1.35; Br, 36.63; N, 12.61.

2-Hydroxy-3-nitro-5-bromo-6-methylpyridine: recrystallized from ethanol as yellow needles, m.p. 221–223°, yield 35%. Diazotization in concentrated sulfuric acid gave only a small amount of product, but it was identical with the product prepared by direct bromination. *Anal.* Calcd. for $C_6H_5O_3N_2Br$: C, 30.91; H, 2.14; Br, 34.41; N, 11.99. Found: C, 30.51; H, 2.16; Br, 34.50; N, 12.58.

2-Hydroxy-3-bromo-5-nitro-6-methylpyridine: recrystallized from ethanol as colorless needles, m.p. 262–264°, yield 60%; also obtained by diazotization of the amino compound but in poor yield. Parker and Shive[6] reported 261°.

(3) A. H. Berrie, G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 2042 (1952).

(4) F. H. Case, THIS JOURNAL, **68**, 2574 (1946).

(5) R. Adams and A. W. Schrecker, *ibid.*, **71**, 1186 (1949).

(6) E. D. Parker and W. Sbive, *ibid.*, **69**, 63 (1947).

(7) Y. Yamamoto, *J. Pharm. Soc. Japan*, **71**, 662 (1951).

(8) This compound is mentioned by Berrie, *et al.*, but it is not characterized, nor bave we been able to find it elsewhere in tbe literature.

(9) This compound has not been reported previously. It was obtained by bromination of 2-bydroxy-5-nitropyridine in acetic acid and melted at 216–218°.

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Carbohydrates in Hazel (*Corylus sp.*). I. Major Sugar Component in Turkish Hazelnut Kernel

BY J. CERBULIS[1]

RECEIVED JUNE 11, 1955

Corylus Avellana is often abundant in Britain and Northern Europe, either as a bush or as a small tree, in woods and thickets. It is cultivated in many countries. Many hybrids of *C. Avellana* and *C. colurna* are cultivated in Turkey. The nut kernel is widely used for food and for the manufacture of nut chocolate and other types of confectionery.[2]

(1) 2848 N. Park Ave., Philadelphia 32, Pa.

(2) F. N. Howes, "Nuts," Faber and Faber Limited, London, 1948, p. 142.