benzene. The solid material (10.6 g., 40%) melted at 108–110° dec. after recrystallization from diisopropyl ether.[7]

Anal. Calcd. for $C_{15}H_{21}O_3N$: C, 68.41; H, 8.04; neut. equiv., 263.3. Found: C, 68.51; H, 7.83; neut. equiv., 264.0.

The benzene wash solution was evaporated to dryness and the residue was extracted with 150 cc. of petroleum ether (30–40°). After removal of the solvent from the extract, there was obtained 4.8 g. (25%) of α-phenylisocaproic acid, m.p. and mixed m.p. 77–78° after recrystallization from petroleum ether (40–60°).

(B) **From α-Phenylisocaproic Acid.**—Isopropylmagnesium chloride, obtained from 1.6 g. of magnesium, 8 cc. of isopropyl chloride and 25 cc. of ether, was stirred, a solution of 5.7 g. of α-phenylisocaproic acid in 150 cc. of benzene was added and the mixture was refluxed for 18 hours. Ethyl isocyanate (2.6 g.), dissolved in 50 cc. of benzene, was added and the mixture was refluxed for 4 hours. The mixture was treated in the manner described above; yield 1.1 g., m.p. and mixed m.p. 108–110° dec. after recrystallization from diisopropyl ether. Calcd. for $C_{15}H_{21}O_3N$: neut. equiv., 263.3. Found: neut. equiv., 263.8.

α-Phenyl-N-ethylisocaproamide (III).—When α-phenyl-α-(ethylcarbamyl)-isocaproic acid (II) was heated in an oil-bath (125°) for 1 hour, carbon dioxide was evolved. The solidified residue was recrystallized from petroleum ether (30–40°); m.p. 64–66°.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.67; H, 9.65. Found: C, 76.70; H, 9.56.

The amide also was prepared by successive treatment of I with thionyl chloride and aqueous ethylamine; m.p. and mixed m.p. 64–66° after recrystallization from petroleum ether (30–40°).

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[7] A positive qualitative test for nitrogen was obtained.

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The Base-catalyzed Cleavage of 2,2-Dialkyl-1,3-diols

BY KENT C. BRANNOCK AND GERALD R. LAPPIN

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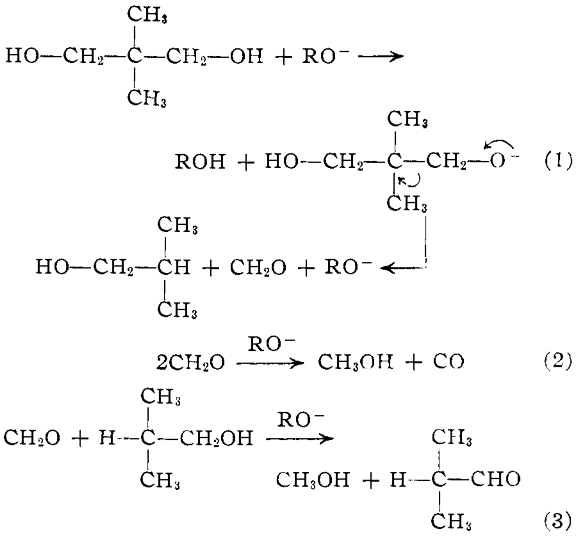
The cleavage of a 1,3-diol by heating with a base was first observed by Nef[1] who heated the sodium salt of 1,3-propanediol at 150° and obtained a small amount of ethyl alcohol and hydrogen. He also heated the diol with an equimolar quantity of sodium hydroxide and obtained a complex mixture of products in which ethyl alcohol, propyl alcohol and acetic acid were identified. The alcohols were presumed to have been formed by the reduction of aldehydes, which were considered to be the primary cleavage products.

More recently, Searles[2] reported an analogous cleavage of 1,3-diols to carbonyl compounds and alcohols when heated at 200° with concentrated aqueous sodium or potassium hydroxide. A hydrogen-bonded cyclic intermediate was proposed to account for this cleavage.

The related base-catalyzed cleavages of β-dimethylaminopivalophenone methiodide,[3] β,β-dimethyl-α-tosyloxy-γ-butyrolactone[4] and 3-bromo-2,2-dimethyl-1-propanol[5] also have been reported.

We wish to report the base-catalyzed cleavage of some 2,2-dialkyl-1,3-diols, which bears a formal resemblance to the cleavages mentioned above. When 2,2-dimethyl-1,3-propanediol was heated with a catalytic amount of dissolved sodium (or with calcium oxide at a slightly higher temperature) cleavage of the diol occurred, presumably according to the scheme



$$HO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}OH + RO^- \longrightarrow ROH + HO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O^- \quad (1)$$

$$\longrightarrow HO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{CH}} + CH_2O + RO^-$$

$$2CH_2O \xrightarrow{RO^-} CH_3OH + CO \quad (2)$$

$$CH_2O + H{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2OH \xrightarrow{RO^-} CH_3OH + H{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CHO \quad (3)$$

The products isolated were isobutyl alcohol, methanol, carbon monoxide and isobutyraldehyde. The carbon monoxide and part of the methanol may have arisen from a Cannizzaro-like disproportionation of formaldehyde or from the base-catalyzed decomposition of the Tishchenko reaction product, methyl formate. The isobutyraldehyde may have arisen from an Oppenauer reaction between isobutyl alcohol and formaldehyde.

Similarly, 2,2-diethyl-1,3-propanediol with dissolved sodium gave 2-ethyl-1-butanol, methanol, carbon monoxide and 2-ethylbutyraldehyde, while 2-methyl-2-propyl-1,3-propanediol gave 2-methyl-1-pentanol, methanol, carbon monoxide and 2-methylvaleraldehyde. The high-boiling residues produced were not investigated.

2,2,4-Trimethyl-1,3-pentanediol, which is unsymmetrical, underwent base-catalyzed cleavage more readily than the propanediols described above. In this case cleavage occurred predominantly at the carbon atom bearing the secondary hydroxyl group and led to the formation of isobutyl alcohol and isobutyraldehyde, although small amounts of the products from cleavage at the primary carbinol carbon were isolated: namely, methanol, carbon monoxide and 2,4-dimethyl-3-pentanone. The 2,4-dimethyl-3-pentanone presumably came from the Oppenauer oxidation of the primary cleavage product, 2,4-dimethyl-3-pentanol, which was not isolated.

Under conditions similar to those which resulted in the cleavage of the 2,2-dialkyl-1,3-diols described above, 2-ethyl-1,3-propanediol, 1,3-propanediol and 1,3-butanediol showed only a negligible amount of decomposition.

The related ester, butyl hydroxypivalate, when heated in the presence of dissolved sodium, under-

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[1] J. U. Nef, *Ann.*, **335**, 302 (1904).

[2] S. Searles and E. K. Ives, Abstracts of Papers, 127th Meeting of the American Chemical Society, 1955, p. 24N.

[3] H. R. Snyder and J. H. Brewster, THIS JOURNAL, **71**, 1061 (1949).

[4] H. Bretschneider and H. Hass, *Monatsh.*, **81**, 945 (1950).

[5] S. Searles and M. J. Gortatowski, THIS JOURNAL, **75**, 3030 (1953).

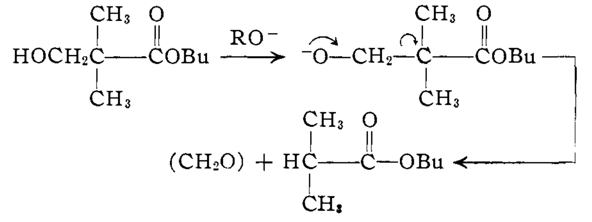
TABLE I

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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Bromination Products of Nitropyridine

BY ELLIS V. BROWN AND HENRY T. BURKE

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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

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

(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).