Alkali Solubility of Alcoholyzed Cellulose.—Hydrolyzed cellulose is known to undergo extensive degradation by hot aqueous alkalies. Data given in Table I show that methanolyzed cotton cellulose does not undergo such an effect. This finding provides support for the view expressed by others that the loss of weight suffered by hydrocellulose in hot, dilute alkali is a function of reactivity, and not of solubility.[12] Alkaline solutions heated with hydrocellulose become discolored, whereas when heated with alcoholyzed cellulose they show no discoloration.

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Dehydrogenation of 1,4-Pentanediol

BY L. P. KYRIDES AND F. B. ZIENTY

The availability of 1,4-pentanediol (I) prompted the study of the dehydrogenation[1] of this glycol. Using a typical copper chromite hydrogenation catalyst,[2] and operating in the liquid phase under reflux, two moles of hydrogen were evolved and γ-valerolactone (II) was produced in 80% yield (an unexpected result). When the reaction mixture was slightly acidified with an organic acid and a downward condenser was used, as much as 30% of γ-acetopropanol[3] (III) was produced together with some (II).

Several derivatives of (III) were prepared (Table I).

TABLE I

Derivative	Recrystn. solvent	M. p.,[a] °C.	Formula	% Nitrogen[b] Calcd.	Found
(I) Bis-*p*-nitrobenzoate	Me_2CO-EtOH	150–151	$C_{19}H_{18}N_2O_8$	7.0	6.8
(III) Semicarbazone	EtOH	154–155[c]	$C_6H_{13}N_3O_2$	26.4	26.5
(III) Thiosemicarbazone	H_2O	102–103	$C_6H_{13}N_3OS$	24.0	23.9
(III) Acetate semicarbazone[d]	H_2O	125–126	$C_8H_{15}N_3O_3$	20.9	21.0
(III) Acetate thiosemicarbazone[d]	MeOH	117–118	$C_8H_{15}N_3O_2S$	19.3	19.3

[a] All melting points are corrected. [b] The analyses were performed by Mrs. J. D. Nevins of the Monsanto Analytical Laboratory. [c] Paul, *Bull. soc. chim.*, **53**, 426 (1933), reported 155–157°. [d] Prepared from (III) acetate, b. p. 88–89° (7 mm.). Slobodin, Zigel and Yanishevskaya, *C. A.*, **39**, 702 (1945), reported b. p. 100–115° (22 mm.). Palomaa, *Chem. Zentr.*, **84**, II, 1959 (1913), reported 211–213°. Bergel, U. S. Patent 2,358,618 (September 19, 1944), reported b. p. 96–99° (12 mm.), 103–104° (14 mm.) and 110–112° (17 mm.).

Experimental

Dehydrogenation of (I). (a) In Absence of Organic Acids.—A mixture of 104 g. (1 mole) of (I), 4 g of copper chromite catalyst[2] and 0.15 g. of powdered reagent sodium hydroxide was stirred vigorously and heated under reflux. At 200° a lively evolution of hydrogen occurred and the temperature soon dropped to 190–192° where the dehydrogenation proceeded smoothly. The evolution of gas (39 liters or two moles on the (I) reacted) ceased in about three hours. The reaction mixture was cooled to about 30°, filtered from the catalyst and distilled under reduced pressure, producing 79 g. (87%) of (II), b. p. 90–92° (16 mm.), $n^{26}D$ 1.4290, d^{25}_4 1.0474, and 12 g. of unreacted (I), b. p. 124–126° (16 mm.) or 120–121° (14 mm.). The (II) was analyzed by titration with alkali.

Anal. Calcd. for $C_5H_8O_2$: mol. wt., 100.1; *MR*, 24.7. Found: mol. wt., 100.0: *MR*, 24.6.

Addition of a small amount of potassium hydroxide, monobasic sodium phosphate, alundum or decolorizing charcoal (Darco) to the reaction mixture produced an 87–90% yield of (II).

(b) **In Presence of Organic Acids.**—Under slightly acid conditions, such as could be attained by the addition of 0.003–0.005 mole per cent. of a non-volatile fatty acid like stearic acid,[1] to the reaction mixture, water and a low-boiling organic material could be distilled off and condensed in appreciable amounts. The mechanism in this reaction probably involves dehydrogenation of the secondary alcohol group in (I) to form (III), which, in its cyclic form,[5] dissociates into water and 2-methyl-4,5-dihydrofuran[6] (IV) which distil over and subsequently recombine to form (III).[7] The reaction of (IV) with water is slow (24–48 hours) and may be accelerated by stirring, but will proceed instantly, and even with violence, in the presence of a small amount of mineral acid, such as hydrochloric acid.

In order to separate the (III) from the (II) formed in the reaction, the crude reaction products were distilled slowly at atmospheric pressure using a short column. The volatile dissociation products of (III) distilled over, leaving the (II) behind in the still. (II) and (III) have similar boiling points under atmospheric pressure.

Reaction in an atmosphere of hydrogen was without benefit in producing (III). Activated copper made by decomposition of cupric carbonate in (I) caused some dehydrogenation to (II), but no (III) was obtained. A nickel hydrogenation catalyst caused extensive dehydration of (I), and produced only about 15% of (III).

(1) Kyrides and Zienty, U. S. Patent 2,382,071 (August 14, 1945); *C. A.*, **40**, 90 (1946).

(2) Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

(3) Several other examples of the formation of keto alcohols by dehydrogenation of glycols are described in the literature: McNamee and Blair, U. S. Patent 2,143,383 (January 10, 1939), *Chem. Zentr.*, **110**, I, 4842 (1939); Hilger, U. S. Patent 1,955,882 (April 24, 1934), see *Chem. Zentr.*, **104**, 1, 2172 (1933); Neish, *Can. J. Research*, **23B**, 67 (1945); Holmes, U. S. Patent 2,036,940 (April 7, 1936), *Chem. Zentr.*, **107**, II, 402 (1936).

(4) Schuette and Sah, THIS JOURNAL, **48**, 3165 (1926), reported $n^{25}D$ 1.4301 and d^{25} 1.04608.

(5) Buchman, THIS JOURNAL, **58**, 1804 (1936).

(6) Lipp, *Ber.*, **22**, 1199 (1889).

(7) Marshall and Perkin, *J. Chem. Soc.*, **59**, 882 (1891). Paul, *Bull. soc. chim.*, **53**, 419 (1933), produced γ-acetopropanol by addition of water to 2-methylene-tetrahydrofuran in the presence of sulfuric acid. Knunyantz, Chelintzev, and Osetrova, *C. A.*, **28**, 4382 (1934), reported b. p. 115–116° (30 mm.) for γ-acetopropanol, while we found b. p. 85–86° (10 mm.)

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Solubility Product of Silver Selenocyanate at 25°

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Subsequent to studies dealing with selenocyanic acid and the gravimetric analysis of $SeCN^-$ as silver selenocyanate (AgSeCN)[1] it became of interest to determine the solubility of this silver salt.

A solubility product of 6.9×10^{-15} (K_{sp} average of four determinations) was found for silver selenocyanate at 25 ± 0.1° using the cell: Ag/

(1) Waitkins, M. S. Thesis, Syracuse University, 1934.