sulfuric acid was added dropwise to a stirred solution of 10.3 g. (0.1 mole) of benzonitrile dissolved in 250 ml. of 1.0*N* hydrazoic acid in benzene. After an elapsed time of 3 hr. the reaction mixture was poured over 100 g. of crushed ice. The aqueous layer was neutralized with 40% sodium hydroxide solution causing the separation of a crude crystalline solid. A single recrystallization from ethanol gave 5.9 g. (37%) of 1-phenyl-5-aminotetrazole; m.p. 160.5–161.5° (reported[7] 159.5–160°).

Anal. Calcd. for $C_7H_7N_5$: N, 43.5. Found: 43.7.

1-Phenyl-5-aminotetrazole from benzaldehyde. Under reaction conditions similar to those described above, 10.6 g. (0.1 mole) of benzaldehyde dissolved in 330 ml. of 1.0 *N* hydrazoic acid in benzene solution was treated dropwise with 40 g. of concentrated sulfuric acid. The temperature of the reaction mixture was maintained at 35–40° for 5 hr. during which gas evolution ceased. The greenish colored reaction mixture was poured over ice and the product was isolated as described in the preceding procedure. After a single recrystallization from ethanol there was received 4.7 g. (30%) of 1-phenyl-5-aminotetrazole; m.p. 159.5–160.5°.

Anal. Calcd. for $C_7H_7N_5$: N, 43.5. Found: 43.4.

Mixtures of 1-phenyl-5-aminotetrazole prepared from benzonitrile and benzaldehyde had m.p. 160°–160.5°.

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Reaction of Silver 4-Hydroxyvalerate with Bromine

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In the course of other work in this laboratory the conversion of *cis*-2-hydroxycyclopentaneacetic acid to *cis*-2-methylcyclopentanol by way of the Hunsdiecker silver salt–bromine degradation was attempted. No carbon dioxide was evolved. Although Oldham and Ubbelohde[2] have suggested that hydroxylic compounds other than water might prevent the decarboxylation reaction from taking place, no investigation appears to have been made of the claim of Hunsdiecker, Hunsdiecker, and Vogt[3] that the reaction proceeds normally with hydroxy acids in which the hydroxyl group is not in the α- position to form hydroxyalkylhalides poorer by one C-atom.

When the reaction of methyl silver adipate with bromine,[4] which in this laboratory gave a 63% yield of methyl 5-bromovalerate, was carried out in the presence, of an equimolar quantity of cyclopentanol, little, if any, carbon dioxide was evolved and none of the desired product was obtained. The cyclopentanol contained 0.088% water; addition of three times this amount of water did not prevent decarboxylation although the yield of methyl 5-bromovalerate was only 43%. Therefore an alcoholic hydroxyl group does indeed prevent decarboxylation.

To determine what products are formed by the reaction of the silver salt of a hydroxy acid in which the hydroxyl group is not in the α- position with bromine, the reaction of silver 4-hydroxyvalerate, prepared from commercially available γ-valerolactone, was investigated. By the salt-to-bromine addition method at 0° a 36% yield of levulinic acid and a 23% yield of γ-valerolactone were obtained along with a small amount of a volatile organic acid which was not identified. No carbon dioxide was formed. By the bromine-to-salt addition method in refluxing carbon tetrachloride the yield of levulinic acid was 18% and of γ-valerolactone 46%. In addition to the small amount of volatile acid, a small quantity of a neutral material, which decomposed on distillation, was formed and a maximum of 2.5% of carbon dioxide was evolved. In both cases the remainder of the product was nonvolatile and acidic and may well have consisted largely of levulinic acid.

EXPERIMENTAL[5]

Reaction of silver 4-hydroxyvalerate with bromine. A solution of 19.8 g. (0.30 mole) of potassium hydroxide in 90 ml. of water was refluxed for one hour with 28 ml. (0.30 mole) of γ-valerolactone. The solution was then cooled and neutralized to *p*H 8 with a few drops of 6*N* nitric acid and a solution of 51.0 g. (0.30 mole) of silver nitrate in 60 ml. of water was added rapidly with stirring and cooling. After about 10 min. the silver 4-hydroxyvalerate was collected on a Büchner funnel and sucked as dry as possible. It was then washed thoroughly by trituration first with methyl alcohol and then with ether, removing the solvents by suction filtration, and dried 24 hr. at room temperature[6] in a vacuum desiccator over Drierite at <1 mm. in the dark. A 90% yield was obtained.

The silver salt (0.27 mole) was finely powdered, placed in the flask from which it was to be added, and dried another 24 hr. over phosphorus pentoxide instead of Drierite. It was then added in small portions to a stirred solution of *ca.* 16 ml. (0.31 mole) of dry[7] bromine in 150 ml. of dry[8] carbon tetrachloride cooling in an ice bath during a period of 70 min. After addition of the silver salt was complete, the reaction mixture was allowed to warm to room temperature. No carbon dioxide was detected when the flask was swept out with dry, carbon dioxide-free nitrogen, which was then passed through a weighed Ascarite tube. The silver bromide was isolated by filtration, washed thoroughly first with hot carbon tetrachloride and then with water, and air-dried; the yield was 94%.

The excess bromine was destroyed with sodium bisulfite and the carbon tetrachloride solutions were washed with an

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[1] Inquiries should be addressed to this author at 211 Scherrer St., Cranford, N. J.

[2] J. W. H. Oldham and A. R. Ubbelohde, *J. Chem. Soc.*, 368 (1941).

[3] H. Hunsdiecker, C. Hunsdiecker, and E. Vogt, U. S. Patent **2,176,181** (1939).

[4] C. F. H. Allen and C. V. Wilson, *Org. Syntheses*, **Coll. Vol. 3,** 578 (1955).

[5] Melting points were determined in open borosilicate glass capillaries using a Hershberg apparatus and are corrected unless otherwise noted.

[6] Silver 4-hydroxyvalerate darkens rapidly when heated.

[7] Bromine was dried by shaking with concentrated sulfuric acid followed by distillation from phosphorus pentoxide.

[8] Carbon tetrachloride was dried by distillation and stored over phosphorus pentoxide.

excess of cold 20% potassium carbonate. The aqueous solutions, which were kept cold, were saturated with potassium carbonate and extracted with carbon tetrachloride. The carbon tetrachloride solutions were combined, dried for 1 hr. over potassium carbonate, and fractionated with a Holzman column at atmospheric pressure. After removal of the carbon tetrachloride, 0.6 g. of material boiling between 77.0° and 200° was obtained. The residue was distilled from a Claisen flask at reduced pressure. A 23% yield of γ-valerolactone was obtained, b.p. *ca.* 92.5–94° (19 mm.); n_D^{25} 1.4326.

Anal. Calcd. for $C_5H_8O_2$: Sapon. equiv., 100. Found: Sapon. equiv., 98.

The phenylhydrazide, prepared according to the procedure given by Huntress and Mulliken,[9] melted at 76.0–77.0°. The phenylhydrazide of an authentic sample of γ-valerolactone, b.p. *ca.* 96° (21 mm.), n_D^{25} 1.4319, was obtained in the same yield and melted at 76.8–77.0°. The melting point of a mixture of the two derivatives was not depressed.

Only 0.6 g. of material remained in the flask at the end of the distillation.

The water layers were strongly acidified with phosphoric acid and steam distilled. The first two liters of steam distillate contained sulfur dioxide, but gave negative tests[10] for halide, phosphate, and a sulfate and the sodium salt gave negative tests for carbonate and nitrate and burned on ignition. The sulfur dioxide was determined as described by Treadwell and Hall[11] and the acidity due to it was subtracted from the total acidity to obtain the amount of organic acid. The first liter of steam distillate contained 17.2 meq. of organic acid, the second 1.7, the third 1.3, and the fourth 1.1 making a total of 21.3 meq. or an 8% yield of volatile acid. Since this acid was undoubtedly contaminated with levulinic acid, which is slightly volatile with steam, and the amount formed was small, it was not identified and steam distillation was stopped. Water was removed at water pump pressure and the residue was extracted with boiling benzene. Distillation of the benzene extract gave 8.1 g. (26%) of levulinic acid, b.p. *ca.* 150–152.5° (20 mm.).

Anal. Calcd. for $C_5H_8O_3$: Neut. equiv., 116. Found: Neut. equiv., 118.

The 2,4-dinitrophenylhydrazone, which was prepared according to the procedure of Cowley and Schuette,[12] melted at 206.6° (uncorr.). The 2,4-dinitrophenylhydrazone of an authentic sample of levulinic acid, b.p. *ca.* 150–151° (20 mm.), melted at 206.6° (uncorr.). The melting point of a mixture of the two derivatives showed no depression.

Only 0.7 g. of material remained in the pot at the end of the distillation.

An additional 10% of levulinic acid was obtained from the residue by extraction with alcohol.

When the reaction was carried out by adding bromine to a stirred suspension of 0.27 mole of silver salt in 150 ml. of carbon tetrachloride without cooling, a mildly exothermic reaction occurred. About 8 ml. (0.16 mole) of bromine was required to give a permanent yellow color; it was added over a period of 42 min. The reaction mixture was then refluxed for 30 min. Three tenths of a gram of material was absorbed on the Ascarite which corresponds to a 2.5% yield of carbon dioxide. However, some of this material was probably bromine as a little bromine vapor was swept through the absorption tube. (Some carbon dioxide was formed as in a similar experiment where the vapors were passed through lime water, the lime water turned milky.) The reaction mixture was worked up as described above; a 94% yield of silver bromide was obtained. The following fractions were obtained from the carbon tetrachloride solutions: 0.9 g. b.p. 80–90°; 1.8 g., b.p. 90–110° (decomp.); 0.4 g., b.p. 110–193°. Distillation of the residue gave a 46% yield of γ-valerolactone, b.p. *ca.* 95–105° (20 mm.). A 7% yield of volatile acid was obtained. Distillation of the benzene extract gave 5.7 g. (18%) of impure levulinic acid, b.p. *ca.* 148–158° (20 mm.); 2.0 g. of material remained in the pot. An attempt to isolate more levulinic acid from the residue by extraction with alcohol was unsuccessful.

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[10] C. H. Sorum, *Introduction to Semimicro Qualitative Analysis*, Prentice-Hall, Inc., New York, 1949, pp. 152–161.

[11] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 9th English ed., John Wiley and Sons, Inc., New York, 1942, p. 322.

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Ketone Condensations Using a Sulfonic Acid Ion Exchange Resin

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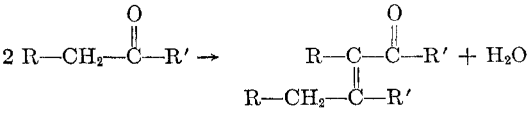
The self-condensation of ketones to α,β-unsaturated ketones has been carried out using numerous catalysts. Wayne and Adkins[1] list (with references) 14 different reagents used to catalyze this type of condensation. The first to use cation exchange resin as a condensation catalyst was Durr.[2] He used Amberlite IR 120 and reported the condensation of cyclohexanone to 2-cyclohexylidenecyclohexanone in 20% yield. Reese[3] showed that the acid catalyzed condensation of cyclohexanone gave 2-(1-cyclohexenyl)cyclohexanone. This was found to be the main product of the Dowex 50 catalyzed condensation of cyclohexanone and was probably what Durr had rather than 2-cyclohexylidenecyclohexanone. Klein and Banchero[4] determined the reaction rate for the condensation of acetone directly to mesityl oxide using a sulfonic acid cation exchange resin (Dowex 50) as the catalyst.

Additional work has been carried out using the above two ketones and three other ketones. With the exception of cyclohexanone, the following general equation illustrates the condensation:



$$2\,R{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}R' \rightarrow R{-}\underset{\underset{R{-}CH_2{-}C{-}R'}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}R' + H_2O$$

The reaction rates are low and long periods of time are required. However, this is counterbalanced by the simplicity of the technique and by the good yields obtained.

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[4] F. G. Klein and J. T. Banchero, *Ind. Eng. Chem.*, **48**, 1278 (1956).