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.

CARR LABORATORY
MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASS.

---

[9] E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds Order I*, John Wiley and Sons, Inc., New York, 1941, p. 353.

[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.

[12] M. A. Cowley and H. A. Schuette, *J. Am. Chem. Soc.*, **55**, 3463 (1933).

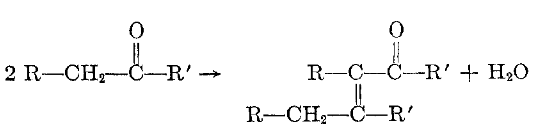
Ketone Condensations Using a Sulfonic Acid Ion Exchange Resin

N. B. LORETTE

Received September 4, 1956

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:



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

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.

---

[1] W. Wayne and H. Adkins, *J. Am. Chem. Soc.*, **62**, 3401(1940).

[2] G. Durr, *Compt. rend.*, **236**, 1571 (1953).

[3] J. Reese, *Ber.*, **75**, 384 (1942).

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

EXPERIMENTAL

Acetone. Twelve hundred g. of acetone (commercial grade) was charged in a 2-l. distillation pot which was equipped with a thermowell and an inlet tube. The pot was attached to a 30-in. column. Between the overhead discharge of the column and the pot inlet tube was placed a catalyst bed. This consisted of 500 ml. of acetone-washed Dowex 50 (hydrogen form) in an insulated 45 × 450 mm. borosilicate glass tube. Boiling of the pot material caused the acetone vapors to pass through the column, over the catalyst and back into the distillation pot. The initial rate of acetone passing over the catalyst was 300 ml. per hour. The rate became lower as the acetone concentration diminished. Progress of the reaction was followed by the rise in pot temperature. At the beginning of the run the pot temperature was 57.8°, while at the end of the run (117 hr.) it was 87°. Distillation of the crude products gave 152 g. of acetone, 464 g. of mesityl oxide–water azeotrope, and 399 g. of mesityl oxide. This is an acetone conversion of 87.4% and a yield of mesityl oxide of 79.4% based on converted acetone.

Ethyl methyl ketone. This ketone was condensed using the same procedure and apparatus that was used for acetone. Eleven hundred ninety-six g. of ethyl methyl ketone was used. The hot vapors maintained a resin bed temperature of 70–80°. After 50 hr. the pot temperature had risen only 3.6°. (The water formed during the condensation was being recycled over the resin by means of the ethyl methyl ketone–water azeotrope, thereby inhibiting further condensation.) By distillation, 942 g. of ethyl methyl ketone and 199 g. of C_8 unsaturated ketone boiling from 77 to 83° at 50 mm. was recovered. The C_8 cut, which was a mixture of the two possible isomers, 5-methyl-4-hepten-3-one and 3,4-dimethyl-3-hexen-2-one, was redistilled at atmospheric pressure. It boiled at 155 to 167°. Molecular weight determination (by benzene freezing point depression) of a cut boiling at 158 to 161° was 127, for a cut boiling at 165 to 167° was 130; theoretical is 126. The refractive index ranged from n_D^{23} 1.4405 for the 155° material to n_D^{23} 1.4460 for the 165 to 167° cut. No effort was made to separate the two isomers quantitatively.

3-Pentanone. Twenty g. of Dowex 50 (hydrogen form) and 660 g. of 3-pentanone were placed in a 1-l. flask equipped with a magnetic stirrer and heated by the top half of a Glas-Col hemispherical heating mantle (to prevent bumping). The pot was attached to a 30-in. column. A system pressure of 200 to 300 mm. was maintained so that boiling could occur without the pot temperature reaching a point where the resin would decompose. This pressure effected pot temperatures of 50 to 75°. The system was operated under total reflux most of the time. Periodically 3-pentanone-water azeotrope cuts of 5 to 20 ml. were taken. After 54 hr. the reaction was stopped and the pot material freed of the catalyst by filtration. Distillation of the filtrate yielded 537 g. of 3-pentanone and 56 g. of 5-ethyl-4-methyl-4-hepten-3-one, b.p. 84–86° at 20 mm, d_{24} 0.856; lit.[1] b.p. 101–104° at 44 mm., d_4^{25} 0.8552.

Cyclohexanone. Twenty-one g. of dry Dowex 50 (hydrogen form) and 545 g. of cyclohexanone were charged in a 1-l., 3-necked flask equipped with a thermometer, condenser, outlet tube, and magnetic stirrer. A pot temperature of 70 to 80° was maintained. About 3 times each day for 1-hr. periods dry ($CaCl_2$) air was drawn in through the condenser, above the liquid and out the outlet tube into a dry ice trap. Water and cyclohexanone vapors were condensed forming two layers. The cyclohexanone was separated and returned to the reaction pot. During the 51.5-hr. run, progress of the reaction was followed by the refractive index change. The initial reading was n_D^{25} 1.4472 and the final was n_D^{25} 1.4960. Distillation of the filtered products yielded 142 g. of cyclohexanone and 268 g. of 2-(1-cyclohexenyl)cyclohexanone, b.p. 125° at 7 mm.; n_D^{18} 1.5072, n_D^{60} 1.4912; lit.[4], n_D^{60} 1.4918.

Acetophenone. Twenty-three g. of Dowex 50 (hydrogen form) and 618 g. of acetophenone were charged in a one-liter, 3-necked flask equipped with a magnetic stirrer. The reaction mixture was maintained at 70–75°. Water was removed from the reaction mixture as in the manner described for cyclohexanone. The refractive index of the mixture increased from an initial n_D^{25} 1.5310 to n_D^{25} 1.5670 after 246 hr. The crude products were freed of the resin by filtration and then distilled to yield 361 g. of acetophenone and 140 g. of yellow dypnone, b.p. 136–139° at 1 mm.; lit.[1] b.p. 138–140° at 1 mm. On cooling, 50 g. of 1,3,5-triphenylbenzene (m.p. 169°) precipitated from the distillation residue.

ORGANIC BASIC RESEARCH LABORATORY
THE DOW CHEMICAL COMPANY
FREEPORT, TEX.

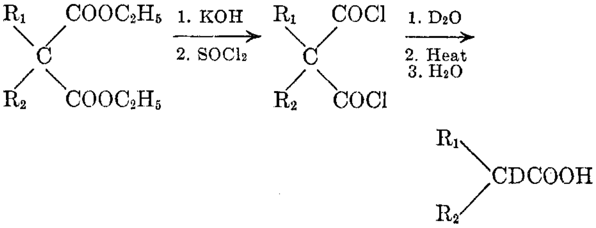
Convenient Preparation of α-Deuterated Acids[1]

CHARLES C. PRICE,[2] ERNEST L. ELIEL,[3] AND ROBERT J. CONVERY

Received September 10, 1956

The conversion of malonic acids to the acid chlorides, followed by hydrolysis with heavy water and decarboxylation, affords a convenient procedure for the preparation of α-deuterated aliphatic and alicyclic acids offering advantages over previous procedures.[4]

α-Deutero-isobutyric and -hexahydrobenzoic acid have been prepared by the following sequence of reactions:



The yields and properties of the intermediate compounds and final products are listed in Table I.

The deuterated acids were found to have some marked differences in infrared spectra from the unlabeled analogs. These data will be presented elsewhere.

---

[1] (1) Abstracted in part from the Master's Dissertation of R. J. Convery, University of Notre Dame, Notre Dame, Ind., supported in part by the Radiation Project, University of Notre Dame, through A.E.C. Contract No. At(11-1)-38.

[2] (2) Present address, University of Pennsylvania, Philadelphia 4, Pa.

[3] (3) Present address, University of Notre Dame, Notre Dame, Ind.

[4] (4) C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 3686 (1953); D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge, and C. R. Hauser, *J. Am. Chem. Soc.*, **76**, 5129 (1954).