

gave 0.4 g. of white crystalline material, m.p. 211–213°. The melting point was not lowered by mixing with an authentic sample of phenylacetylurea (m.p. 211–213°) pre-

pared from phenylacetyl chloride and urea. *Anal.* Calcd. for  $C_9H_{10}O_2N_2$ : N, 15.73. Found: N, 15.51.  
NEWARK, DELAWARE

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

## Cyclization and Decarboxylation of $\alpha$ -Hydromucic Acids

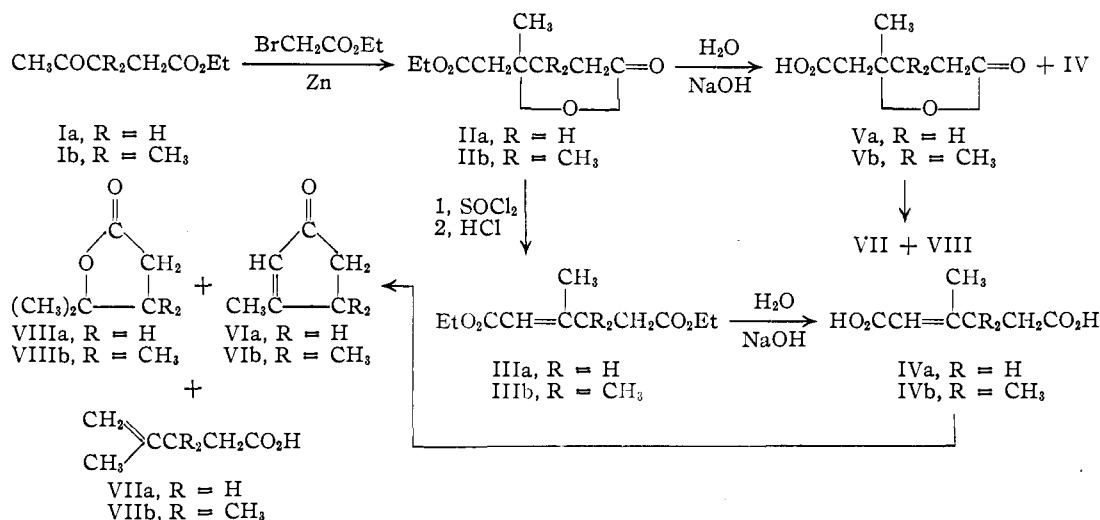
BY HENRY E. BAUMGARTEN

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The thermal decarboxylation of  $\beta$ -methyl- $\alpha$ -hydromucic acid (IVa) yields 4-methyl-4-pentenoic acid (VIIa) and  $\gamma$ -methyl- $\gamma$ -valerolactone (VIIIa). Thermal decarboxylation of  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromucic acid (IVb) yields largely  $\beta,\beta,\gamma$ -trimethyl- $\gamma$ -valerolactone (VIIIb). Thermal cyclization and decarboxylation of the barium salts of the foregoing  $\alpha$ -hydromucic acids yields 3-methyl-2-cyclopentenone (VIa) and 3,4,4-trimethyl-2-cyclopentenone (VIb), respectively. A mechanistic interpretation of some of these reactions is suggested.

In an earlier communication<sup>1</sup> we described an apparently general procedure for the synthesis of certain alkylcyclopentanones which included as an important part the sequence I  $\rightarrow$  V, illustrated in the flow sheet. Hydrogenation of the  $\alpha$ -hydromucic acid (IV) to the substituted adipic acid and

and condensation products of the ketone). This communication reports, as an extension of our earlier work, the results of a study of the cyclization and decarboxylation of  $\beta$ -methyl- $\alpha$ -hydromucic acid (IVa) and  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromucic acid (IVb).



cyclization of the latter constituted the remainder of the synthesis. We acknowledged at that time that a similar procedure, differing in that cyclization to a cyclopentenone preceded hydrogenation, had been utilized earlier by Okazaki.<sup>2,3</sup> Even earlier Ruzicka<sup>4</sup> had shown that distillation of the anhydrides of 3-heptenedioic acids (or treatment of their esters with sodium) gave low yields of cyclohexenones, and Merejkowsky<sup>5</sup> had reported that, although slow distillation of  $\beta$ -hydromucic acid gave a good yield of 2-pentenoic acid and no cyclopentenone, distillation of the calcium salt of the acid gave a low yield of cyclopentenone (accompanied by 1,3-butadiene, carbon monoxide

The acids IVa and IVb were prepared as indicated in the flow sheet. The procedure was described in detail (for IVb) in the earlier report.<sup>1</sup> In that report it was stated that the direct alkaline hydrolysis of the lactonic ester IIb gave a mixture of products, the solid acid IVb and a liquid assumed but not proved to be the lactonic acid Vb, in roughly equal amounts. In this work the similar hydrolysis of IIa gave at most 15% of the solid acid IVa, the remainder of the product being a non-crystallizable liquid. Fortunately, in this later work it was possible to distil the liquid under reduced pressure with only slight decomposition. Elementary analysis and neutralization equivalent data on the distilled liquid support fairly well the lactonic acid structure, Va.

When the acid IVa was heated with a trace of manganous carbonate, a trace of barium hydroxide, or an equivalent amount of either (conditions usually conducive to the cyclization of adipic acids), decarboxylation began at about 220° accompanied by distillation of a liquid product containing only a trace of 3-methyl-2-cyclopenten-

(1) H. E. Baumgarten and D. C. Gleason, *J. Org. Chem.*, **16**, 1658 (1951).

(2) K. Okazaki, *J. Pharm. Soc. Japan*, **63**, 629 (1943); *C. A.*, **45**, 188 (1951).

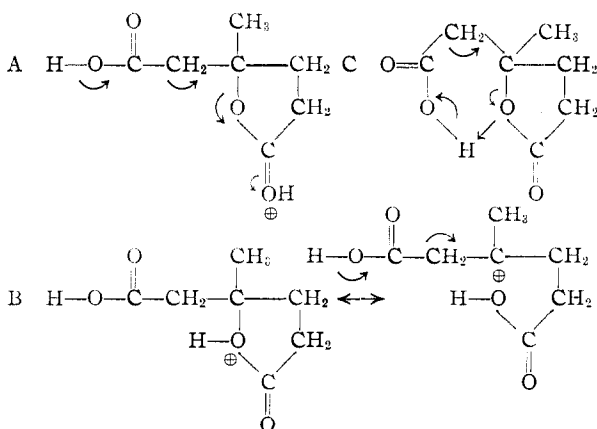
(3) The original paper of Okazaki is not currently available to us and, unfortunately, the abstract (ref. 2) of his work is both so unusually brief and so garbled by typographical errors that it is not clear to us whether Okazaki cyclized the equivalent of IV or of V (as the barium salt).

(4) L. Ruzicka, *Helv. Chim. Acta*, **2**, 144 (1919).

(5) B. K. Merejkowsky, *Bull. soc. chim.*, [4], **37**, 1174 (1925).

tenone (VIa) and consisting principally of 4-methyl-4-pentenoic acid (VIIa) and  $\gamma$ -methyl- $\gamma$ -valerolactone (VIIIa). The identity of the latter was readily established by comparison with the known substance.<sup>6,7,8</sup> The structure of the former was assigned tentatively on the basis of (a) hydrogenation of the unsaturated acid to isocaproic acid and (b) oxidation of the unsaturated acid with potassium permanganate to levulinic acid, isolated in low yield and identified through the *p*-nitrophenylhydrazine. The same mixture of products (VIIa and VIIIa) was obtained when IVa was heated in the absence of added catalysts, and it was found that the relative amounts of VIIa and VIIIa in the product varied with the rate of heating, VIIa being formed in larger amount on rapid heating. On slow distillation at atmospheric pressure or on long standing VIIa partially lactonized to VIIIa, whereas VIIIa could be distilled at atmospheric pressure with no detectable change into VIIa. These results suggest that VIIa is the precursor of VIIIa in the decarboxylation process and are in agreement with the conclusions reached by Johnson and Hunt<sup>9</sup> in their study of the decarboxylation of paraconic acids to lactones and unsaturated acids.

Assuming that VIIa is the most immediate isolable product of the decarboxylation of IVa, there are two reasonable general pathways leading from IVa to VIIa. First, IVa may decompose according to the general mechanism proposed by Arnold, Elmer and Dodson<sup>10</sup> for the decarboxylation of  $\alpha,\beta$ -unsaturated acids (through isomerization to the  $\beta,\gamma$ -unsaturated acid followed by decarboxylation through a cyclic transition complex). Or, second, lactonization of IVa to Va may be the initial step, followed by acid-catalyzed decarboxylation similar to that proposed by Johnson and Hunt<sup>9</sup> for the paraconic acids. Thus, three schemes for the decomposition of Va may be written which are quite similar to the three transitions proposed by Johnson and Hunt, two requiring intermolecular acquisition of a proton (A and B) and one intramolecular (C).



(6) R. L. Frank, R. Armstrong, J. Kwiatek and H. A. Price, *THIS JOURNAL*, **70**, 1379 (1948).

(7) S. A. Glickman and A. C. Cope, *ibid.*, **67**, 1012 (1945).

(8) R. P. Linstead, *J. Chem. Soc.*, 115 (1932).

(9) W. S. Johnson and R. H. Hunt, *THIS JOURNAL*, **72**, 935 (1950).

(10) R. T. Arnold, O. C. Elmer and R. M. Dodson, *ibid.*, **72**, 4359 (1950).

All of the suggested schemes for the path of decomposition of IVa lead to the same primary product, VIIa.

When the lactonic acid Va was heated to 220°, decarboxylation occurred readily giving the expected mixture of VIIa and VIIIa. This result gives some support to the second general mechanism for the decarboxylation of IVa (IVa  $\rightarrow$  Va  $\rightarrow$  VIIa  $\rightarrow$  VIIIa), but since it has not been demonstrated that isomerization of Va to IVa does not occur,<sup>11</sup> followed by decarboxylation of the  $\alpha,\beta$ -unsaturated acid according to the Arnold, Elmer and Dodson mechanism, the added evidence cannot be regarded as conclusive.

Thermal decomposition of the acid IVb gave results similar to those obtained with IVa, although the amount of VIIb isolated was very small under all conditions, the principal product being the solid lactone VIIIb. The structure of VIIIb was established by comparison with a specimen prepared by another route.<sup>12</sup> The structure of the acid VIIb was inferred from the work on VIIa, since VIIb could not be isolated and kept free from the lactone VIIIb, complete isomerization usually requiring only one or two days at room temperature.

When IVb was heated in the presence of a slight excess of manganous carbonate, a 22% yield of 3,4,4-trimethyl-2-cyclopentenone (VIb) was obtained; but, when only a small amount of the catalyst was used, only a trace of VIb was formed. When the acids IVa and IVb were converted into the corresponding barium salts and these salts were heated at 300–320°, cyclization and decarboxylation occurred giving 22% and 63%, respectively, of the cyclopentenones, VIa and VIb. The greater yield of the latter may be correlated with the known influence of methyl (or alkyl) groups on the ease of cyclization of dibasic acids.

The results from this and the cited previous studies<sup>9,10</sup> lead one to infer that the thermal decomposition of  $\beta$ -hydromuconic acid should yield as the primary product, not 2-pentenoic acid as reported by Merejkowsky,<sup>5</sup> but 4-pentenoic acid. This inference is currently being studied.

### Experimental<sup>13</sup>

$\delta$ -Carbethoxy- $\gamma$ -methyl- $\gamma$ -valerolactone (IIa) was prepared by a procedure exactly analogous to that for  $\delta$ -carbethoxy- $\beta,\beta,\gamma$ -trimethyl- $\gamma$ -valerolactone<sup>14</sup> (IIb) from 28 g. (2.00 moles) of ethyl levulinate, 367 g. (2.20 moles) of ethyl bromoacetate and 143 g. (2.10 moles) of zinc foil in 800 ml. of benzene and 700 ml. of toluene. The yield of lactone<sup>15</sup> was 130 g. (35%, 40% based on a recovery of 12.5% of the ethyl levulinate), b.p. 103–104° (1 mm.);  $n_D^{25}$  1.4505;  $d_4^{25}$  1.120; calcd. *MR* 44.72, found *MR* 44.72.

(11) The partial isomerization of terebic acid to tereaconic acid during the thermal decarboxylation of the former is a somewhat related example.<sup>5</sup>

(12) The lactone VIIIb was obtained by Mr. D. C. Gleason (M.S. Thesis, University of Nebraska, 1950) as a by-product in the preparation of ethyl  $\beta,\beta$ -dimethyllevulinate from the reaction of  $\beta$ -carbethoxy- $\alpha,\alpha$ -dimethylpropionyl chloride with what was probably a mixture of dimethylcadmium and methylmagnesium iodide.

(13) Elementary analyses by Clark Microanalytical Laboratory, Urbana, Illinois. All melting points are corrected, boiling points, uncorrected.

(14) P. Duden and R. Freytag, *Ber.*, **36**, 953 (1903).

(15) R. Kuhn, F. Kohler and L. Kohler (*Z. physiol. Chem.*, **242**, 171 (1936)) have reported a yield of approximately half that reported here of the corresponding hydroxy diethyl ester and no IIa. On the basis of physical constants, b.p. 108° (0.6 mm.),  $n_D^{15}$  1.4508, however, we believe that their product was actually the lactone, IIa.

*Anal.* Calcd. for  $C_9H_{14}O_4$ : C, 58.05; H, 7.58. Found: C, 58.15; H, 7.45.

Diethyl  $\beta$ -methyl- $\alpha$ -hydromuconate (IIIa) was prepared by refluxing 77.5 g. (0.416 mole) of  $\delta$ -carbethoxy- $\gamma$ -methyl- $\gamma$ -valerolactone with 238 g. (2.0 moles) of thionyl chloride, adding the resultant mixture to 250 ml. of absolute ethanol saturated at 0° with hydrogen chloride, distilling off the ethanol and thermally dehydrohalogenating the residue according to the procedure previously described for diethyl  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromuconate<sup>1,16</sup> (IIIb). Distillation through a 15-in. Vigreux column gave 81.5 g. (87.5%, crude yield 93%) of the ester, b.p. 101–102° (0.5 mm.),  $n_D^{25}$  1.4500,  $d_4^{25}$  1.017.

*Anal.* Calcd. for  $C_{11}H_{18}O_4$ : C, 61.65; H, 8.47. Found: C, 61.21; H, 8.32.

$\beta$ -Methyl- $\alpha$ -hydromuconic Acid (IVa). (A).—To a hot solution of 64 g. (1.6 moles) of sodium hydroxide in 192 g. of water was added a solution of 75 g. (0.35 mole) of diethyl  $\beta$ -methyl- $\alpha$ -hydromuconate in 86 ml. of ethanol. On shaking the mixture boiled vigorously. It was heated under reflux for 1.5 hours, the major portion of the ethanol was distilled off and the residue was chilled in ice and made acid to congo red with hydrochloric acid. No organic layer separated but, on standing overnight in the refrigerator, some solid deposited, which was collected by filtration giving 33 g. (60%) of crude product. The filtrate was extracted with three 100-ml. portions of ether. Evaporation of the ether left a pale yellow liquid, which largely solidified after standing in the refrigerator for three weeks. Recrystallization of the combined solids from benzene gave 41 g. (75%) of  $\beta$ -methyl- $\alpha$ -hydromuconic acid, m.p. 118–120° (not well defined; Penfold, Ramage and Simonsen<sup>17</sup> report m.p. 121–122° with a similar lack of definition and suggest *cis-trans* isomerism as the explanation).

*Anal.* Calcd. for  $C_7H_{10}O_4$ : C, 53.16; H, 6.37. Found: C, 53.38; H, 6.35.

(B).—To a warm solution of 40 g. (1.0 mole) of sodium hydroxide in 120 ml. of water was added 46.5 g. (0.25 mole) of  $\delta$ -carbethoxy- $\gamma$ -methyl- $\gamma$ -valerolactone. A vigorous reaction took place which was completed by heating the mixture under reflux for 1.5 hours. The solution was chilled in ice and made acid to congo red with hydrochloric acid (85 ml.). No solid separated, even after prolonged cooling. The solution was extracted six times with 50-ml. portions of ether. Evaporation of the ether left a liquid which slowly deposited crystals of the desired acid (more rapidly when shaken with petroleum ether). The yield was 5–6 g. (12–15%), m.p. 118–120° after recrystallization from benzene. The aqueous solution was reextracted ten times with 50-ml. portions of ether, the ether was evaporated and the residue (combined with the liquid product above) was distilled from a small claisen flask, giving 20 g. (50%) of  $\delta$ -carboxy- $\gamma$ -methyl- $\gamma$ -valerolactone (Va), b.p. 163–165° (0.5 mm.); calcd. neut. equiv. 158, found neut. equiv. 155.

*Anal.* Calcd. for  $C_7H_{10}O_4$ : C, 53.16; H, 6.37. Found: C, 53.15; H, 6.26.

**Decarboxylations and Cyclizations.** (a) **General Procedure.**—The material to be decomposed, mixed intimately with any catalyst used, was placed in a distillation flask of such size that the mixture, if liquid, filled the flask half full, if solid, two-thirds full. The flask was fitted with a side-arm test-tube or another distilling flask (cooled with ice-water) as a receiver and with a thermometer extending into the reaction mixture. The outlet arm of the receiver was connected through a short piece of tubing to a wash bottle containing 25% more than the theoretical amount of cold 20% sodium hydroxide solution (calculated on the basis of the carbon dioxide and the organic acid expected). The reaction mixture was heated to the desired temperature in an air-bath and the reaction that ensued was allowed to continue as long as any product distilled. The material in the receiver was washed twice with cold 10% sodium bicarbonate solution and once with water. The aqueous solutions (including the sodium hydroxide solution in the wash bottle) were extracted with two portions of ether. The ether was dried over sodium

sulfate and evaporated and the neutral fraction resulting was fractionally distilled under reduced pressure. The aqueous solutions were combined, chilled in ice-salt mixture, and carefully acidified with hydrochloric acid to congo red. The resulting mixture was extracted with four portions of ether, the ether was dried over sodium sulfate and evaporated, and the acid fraction was distilled under reduced pressure.

(b) **Of  $\beta$ -Methyl- $\alpha$ -hydromuconic Acid (IVa).**—In a typical experiment a mixture of 31.6 g. (0.20 mole) of  $\beta$ -methyl- $\alpha$ -hydromuconic acid and 2.6 g. (0.023 mole) of manganese carbonate were decomposed using the above procedure. Decomposition began at about 220° and was continued up to 300°. Distillation of the neutral fraction gave two products. The first, 0.2 g. (1%), b.p. 150–160°, gave a semicarbazone melting at 225–226°, which is in fair agreement with the value, 230°, reported for the semicarbazone of 3-methyl-2-cyclopentenone.<sup>18</sup> The second product, 10 g. (44%), was  $\gamma$ -methyl- $\gamma$ -valerolactone (VIIIa), b.p. 89.5–90° (13 mm.),  $n_D^{25}$  1.4323,  $d_4^{25}$  1.005 (reported values<sup>6,7</sup> are: b.p. 89–91° (17 mm.), 95° (20 mm.),  $n_D^{25}$  1.4312,  $n_D^{20}$  1.4352). When treated with aqueous ammonia following the procedure described by Linstead,<sup>8</sup> the lactone gave the colorless, crystalline  $\gamma$ -hydroxyisocaproamide, m.p. 101–102° (reported<sup>8</sup> m.p. 101°).

The acid fraction, 21.7 g. (12%), b.p. 101.5–103° (14 mm.),  $n_D^{25}$  1.4370, consisted in part, at least, of 4-methyl-4-pentenoic acid (VIIa), as shown below. The acid showed considerable tendency to lactonize (to VIIIa) and most samples, after standing one or two days, contained 5–10% lactone. The physical constants above are for a freshly distilled sample with neutralization equivalent, 116 (calcd. 114). Lactonization was facilitated by warming with a little hydrochloric acid.

The acid rapidly decolorized both bromine in carbon tetrachloride and 1% potassium permanganate solution. Hydrogenation (at 30° and 45 p.s.i.) of 1 g. of the acid in 50 ml. of ethanol over 0.1 g. of platinum oxide was complete in 30 minutes. The ethanolic solution was treated with a small amount of dilute aqueous sodium bicarbonate (to litmus) and the ethanol was evaporated. The saturated acid, isocaproic acid, was liberated from the salt with hydrochloric acid, extracted with ether and freed of ether by evaporation. The acid was converted into isocaproanilide, m.p. 112–112.5° (undepressed by admixture with an authentic sample), in the usual manner *via* the acid chloride.

A 5.0-g. (0.027-mole) sample of the acid (from another decomposition) was dissolved in a solution of 2.3 g. (0.028 mole) of sodium bicarbonate in 200 ml. of water. To this solution, well stirred and chilled in ice to 5°, was added in small amounts 13.8 g. (0.087 mole) of potassium permanganate (the minimum amount to maintain a stable purple color, but less than the calculated amount). After addition the mixture was stirred one hour at the low temperature. The manganese dioxide was filtered off and the solution was acidified with 1:1 sulfuric acid and water. A small amount of color was removed with saturated sodium bisulfite solution. The aqueous solution was extracted in a continuous extractor with methylene chloride for eight hours. Evaporation of the methylene chloride left a small amount of colorless liquid. The liquid reacted instantly with iodine-potassium iodide solution and alkali in the cold with the formation of iodoform. Distillation of half of the liquid gave 0.8 g. of the lactone VIIIa (b.p. 205–207°), about 0.3 g. boiling in the range of levulinic acid (245–250°) and a considerable high-boiling residue. When the undistilled liquid was treated with *p*-nitrophenylhydrazine in 40% acetic acid solution, the *p*-nitrophenylhydrazone formed rapidly at room temperature. One recrystallization from ethanol-water gave the *p*-nitrophenylhydrazone in the form of orange rhombs, m.p. 177–178°, mixed m.p. with authentic levulinic acid *p*-nitrophenylhydrazone, 177–178°.

*Anal.* Calcd. for  $C_{11}H_{18}N_2O_4$ : N, 16.73. Found: N, 16.81.

A 3.0-g. sample of the acid was mixed with 6.0 g. of thionyl chloride in 20 ml. of dry benzene and allowed to stand at room temperature overnight. To this solution was added 5 g. of aniline. The benzene solution was washed with water, dilute hydrochloric acid, water, dilute sodium hydroxide and more water. Evaporation of the benzene left a pasty mass, which, after four recrystallizations from

(16) For the original procedure see: J. Cason, C. E. Adams, L. L. Bennett, Jr., and J. D. Register, *THIS JOURNAL*, **66**, 1674 (1944).

(17) A. R. Penfold, G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.*, 1496 (1939).

(18) M. Godchot and F. Taboury, *Compt. rend.*, **156**, 1779 (1913).

dilute ethanol, gave 1.2 g. of an anilide as fine, white needles, m.p. 107.8–108.4°.

*Anal.* Calcd. for  $C_{12}H_{14}NO$ : C, 76.15; H, 7.99; N, 7.40. Found: C, 76.80; H, 8.01; N, 7.35.

The anilide of 4-methyl-3-pentenoic acid is reported to melt at 106°,<sup>19</sup> and it is possible that migration of the double bond from the 4,5- to the 3,4-position may have occurred under the conditions of the experiment although in several experiments the same anilide was obtained each time. The position of the double bond was not determined, however.

When the decomposition of  $\beta$ -methyl- $\alpha$ -hydromuconic acid was carried out in the absence of any added catalyst, 4-methyl-4-pentenoic acid and  $\gamma$ -methyl- $\gamma$ -valerolactone were obtained in varying amounts depending on the rate at which the products were distilled from the reaction mixture. On rapid distillation yields of up to 39% of the acid were obtained with the total yield of acid and lactone in the range 56–70%.

(c) **Of  $\delta$ -Carboxy- $\gamma$ -methyl- $\gamma$ -valerolactone (Va).**—In a typical experiment 8.0 g. (0.05 mole) of  $\delta$ -carboxy- $\gamma$ -methyl- $\gamma$ -valerolactone was decomposed at 220–280° using the procedure outlined in (a) above. The decomposition was complete in fifteen minutes, giving 6 g. of liquid product. Separation and purification of the fractions as described in (a) above gave 1.9 g. (33%) of  $\gamma$ -methyl- $\gamma$ -valerolactone, 2.1 g. (35%) of 4-methyl-4-pentenoic acid, 0.5 g. of high boiling neutral residue and 1.0 g. of high boiling acid residue.

(d) **Of Mixtures of Acid IVa and Lactone Va.**—For preparative purposes the mixture of  $\delta$ -carboxy- $\gamma$ -methyl- $\gamma$ -valerolactone and  $\beta$ -methyl- $\alpha$ -hydromuconic acid obtained from the hydrolysis of  $\delta$ -carbethoxy- $\gamma$ -methyl- $\gamma$ -valerolactone was decomposed without prior separation. Under these conditions the yield of  $\gamma$ -methyl- $\gamma$ -valerolactone was 20–26% (based on  $\delta$ -carbethoxy- $\gamma$ -methyl- $\gamma$ -valerolactone) and the yield of 4-methyl-4-pentenoic acid was 15–25%.

(e) **Of the Barium Salt of  $\beta$ -Methyl- $\alpha$ -hydromuconic Acid.**—A solution of 35 g. (0.11 mole) of barium hydroxide octahydrate in 500 ml. of water was prepared and boiled briefly to precipitate the barium carbonate present, which was filtered off and discarded. A solution of 11.5 g. (0.073 mole) of  $\beta$ -methyl- $\alpha$ -hydromuconic acid in 100 ml. of water was neutralized with the barium hydroxide solution to phenolphthalein. The water was evaporated on the hot-plate to near dryness. The crude salt that precipitated toward the end of the evaporation process was filtered off and washed with acetone (which also precipitated a small additional amount of salt from the remaining aqueous solution). The crude, moist salt (22.5 g.) was decomposed as described in (a) above at 300–320°, about four hours being required for the process. The crude distillate was washed with 25 ml. of 20% potassium carbonate solution, the aqueous solution was extracted with three 25-ml. portions of ether, the ether was evaporated and the residue from the evaporation was combined with the water-insoluble product and distilled under reduced pressure, giving 1.5 g. (22%) of 3-methyl-2-cyclopentenone (VIa), b.p. 105–110° (90 mm.),  $n_D^{25}$  1.4860. There was some undistillable residue in the flask. For identification the ketone was converted in the usual manner into the semicarbazone, which formed slowly (24 hours) and which was recrystallized from 95% ethanol,

m.p. 226–227° (m.p. tube inserted in bath at 220°, lit.<sup>18</sup> m.p. 230°).

*Anal.* Calcd. for  $C_7H_{11}N_3O$ : C, 54.88; H, 7.24; N, 27.43. Found: C, 55.03; H, 7.51; N, 27.48.

(e) **Of  $\beta,\gamma,\gamma$ -Trimethyl- $\alpha$ -hydromuconic Acid (IVb).**—In a typical decarboxylation, 10 g. (0.054 mole) of  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromuconic acid<sup>1</sup> was decomposed as described in (a) above at about 220°. It was necessary to use a distilling flask with a wide side arm to prevent plugging by the solid product. The largely solid product was washed with a little dilute potassium carbonate and was recrystallized from dilute ethanol, giving 5.5 g. (72%) of  $\beta,\beta,\gamma$ -trimethyl- $\gamma$ -valerolactone (VIIIb), m.p. 99–100°, mixed m.p. with a sample prepared by another route,<sup>12</sup> 99–100°.

*Anal.* Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.92. Found: C, 67.58; H, 9.64.

The potassium carbonate wash water was chilled in ice and acidified to congo red with hydrochloric acid. A small amount of ill-smelling liquid separated that was picked up in ether, dried over sodium sulfate and recovered from the ether by evaporation. After standing overnight, the liquid (presumably 3,3,4-trimethyl-4-pentenoic acid) had completely solidified (to VIIb) and lost its bad odor.

In another experiment, 10 g. (0.054 mole) of  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromuconic acid was mixed with 7 g. (0.06 mole) of manganous carbonate and the mixture was decomposed as described in (a) above. At first a small amount of water distilled, then some of the solid lactone and much more slowly a clear, yellow liquid. About six hours heating at 320–340° was required before the last drops of product were obtained. The liquid product was decanted from the solid, purified as in (a) and distilled under reduced pressure, giving 1.5 g. (22%) of 3,4,4-trimethyl-2-cyclopentenone (VIb), b.p. 100–108° (30 mm.). Distillation of the solid (lactone) gave only a trace of material boiling in the same range. The semicarbazone of the ketone, prepared in the usual manner, melted at 202–203° (lit.<sup>20</sup> m.p. 199.5–200.0°).

When only 1.0 g. of manganous carbonate was substituted for the 7 g. of the preceding experiment, only a trace of the cyclopentenone was obtained, the principal product (72%) being  $\beta,\beta,\gamma$ -trimethyl- $\gamma$ -valerolactone.

(f) **Of the Barium Salt of  $\beta,\gamma,\gamma$ -Trimethyl- $\alpha$ -hydromuconic Acid.**—The crude barium salt (18 g.) of  $\beta,\gamma,\gamma$ -trimethyl- $\alpha$ -hydromuconic acid, prepared as described in (c) above from 10 g. (0.054 mole) of the acid and 35 g. (0.11 mole) of barium hydroxide octahydrate, was decomposed at 300–320° as described in (a) above, the decomposition requiring about six hours. The 4.5 g. of clear, yellow liquid that resulted was twice distilled under reduced pressure, giving 4.3 g. (63%) of 3,4,4-trimethyl-2-cyclopentenone (VIb), b.p. 88–90° (19 mm.),  $n_D^{25}$  1.4698. The semicarbazone of the ketone, prepared in the usual manner and recrystallized from dilute ethanol, melted at 202–203° (dec.) (lit.<sup>20</sup> m.p. 199.5–200.0°).

*Anal.* Calcd. for  $C_9H_{13}N_3O$ : C, 60.32; H, 7.31; N, 23.45. Found: C, 60.53; H, 7.93; N, 23.67.

LINCOLN 8, NEBRASKA

(19) A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2343 (1928).

(20) H. Sargent, *J. Org. Chem.*, 7, 154 (1942).