Evaporative distillation of 2.1 g. of fraction c gave 1.5 g. of material distilling at 45° at 0.05 mm., $n^{25}D$ 1.4952, d^{21} 1.1416, and 0.29 g. of higher boiling liquid. The 2,4-dinitrophenylhydrazone of fraction c was prepared from 0.33 g. of un-redistilled material, giving 0.06 g. of orange needles, m.p. 186–189.5° (rapid heating), m.p. 184–185° dec. after recrystallization from ethanol and then from benzene. A mixed m.p. with the 2,4-dinitrophenylhydrazone of fraction b was 184–185° dec.

A small portion of fraction c was heated with concentrated hydrochloric acid for several hours. Concentration of an ethereal extract of the acidic solution gave an oil which was treated with an alcoholic solution of phenylhydrazine hydrochloride. A small amount of a yellow phenylhydrazone was obtained, which after recrystallization from ethanol melted at 158–159° dec. (reported by Dilthey and Böttler[24] for the phenylhydrazone of phenylglyoxylic acid, m.p. 160–161°).

1,2,3-Triphenylpenten-1-ol Peroxide. (a) Preparation.—1,2,3-Triphenylpenten-1-ol was prepared according to Kohler[13] by instantly treating a moist ethereal solution of the decomposed Grignard addition product of ethylmagnesium bromide and benzaldesoxybenzoin with air. Kohler reported the isolation of two isomers, m.p. 166° and m.p. 109° (no decomposition), neither of which liberated iodine from potassium iodide. Repeated crystallization, first from an acetone–heptane mixture and finally from acetone gave a product, m.p. 149–149.5° dec., which liberated iodine from an alcoholic solution of potassium iodide.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.8; H, 6.4. Found: C, 79.6; H, 6.2.

(b) Cleavage.—A solution of 0.01 mole of potassium *t*-butoxide and 3.46 g. (0.01 mole) of 1,2,3-triphenylpenten-1-ol peroxide in 100 cc. of dry *t*-butyl alcohol was sealed in a bottle under nitrogen, shaken for 2 hr., and then allowed to remain overnight. After neutralization with 2 *N* hydrochloric acid and distillation of the solvent, first water and then ether were added to the solution. The ethereal layer was washed twice with a 2 *N* sodium carbonate solution, the washings being added to the aqueous fraction which was then acidified, yielding 0.52 g. of benzoic acid, m.p. 122–122.5°. Ether extraction of the mother liquor afforded an additional 0.19 g. of acid (total yield 58%). The ethanolic solution of the red oil resulting from concentration of the ethereal fraction yielded 1.27 g. (54% yield) of ethyldesoxybenzoin, m.p. 56–57°, reported m.p. 58°.[25]

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.6; H, 7.1.

NEW YORK 27, NEW YORK

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[24] W. Dilthey and Th. Böttler, *Ber.*, **52**, 2040 (1919).

[25] V. Meyer and L. Oelkers, *ibid.*, **21**, 1295 (1888).

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. XIV.[1] β-Isovalerolactone

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER AND W. L. BEEARS

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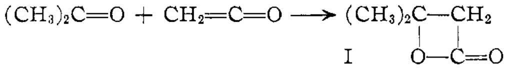
The reactions of β-isovalerolactone are similar to those of β-propiolactone except for a rapid loss of carbon dioxide in polar solvents and a greater difficulty of substitution at the β-tertiary carbon atom. Polymerization, hydrolysis and reactions of β-isovalerolactone with halogen acids, alcohols, phenols, amines, dithiocarbamic acid salts and thionyl chloride are discussed.

In the continuation of our work on β-lactones,[1] it was of interest to compare the reactivity of a β-lactone disubstituted in the β-position. For this purpose, β-isovalerolactone[2] (I) was prepared from ketene and acetone.

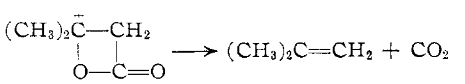


$$(CH_3)_2C{=}O + CH_2{=}C{=}O \longrightarrow \begin{array}{l}(CH_3)_2C\text{—}CH_2\\ \qquad\quad | \qquad |\\ \qquad\quad O\text{—}C{=}O\end{array}$$

I

This β-lactone I exhibits the characteristic shift of carbonyl absorption to shorter wave length,[3] and is reasonably stable at ordinary temperatures.

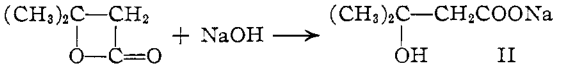
In water at room temperature, I decomposes rapidly to carbon dioxide and isobutylene to the near exclusion of hydrolysis. This is probably due to a tendency for ionization at the tertiary carbon–oxygen bond with subsequent shift of electrons and expulsion of carbon dioxide occurring more rapidly



$$\begin{array}{l}(CH_3)_2\overset{+}{C}\text{—}CH_2\\ \qquad\quad | \qquad |\\ \qquad\quad \underset{-}{O}\text{—}C{=}O\end{array} \longrightarrow (CH_3)_2C{=}CH_2 + CO_2$$

than attack of an ion at the tertiary carbon. This ease of loss of carbon dioxide in polar solvents and the difficulty of attack at the β-tertiary carbon atom limits the yields of products obtained by this type of reaction. These are the only significant differences in the reactions of I as compared to the unsubstituted β-lactone. Reactions due to attack at the carbonyl group with ordinary ester type ring opening occur in a normal manner.

The very rapid reaction of hydroxyl ion with β-propiolactone is attributed[4] to normal ester hydrolysis at the carbonyl group. This interpretation is confirmed by the hydrolysis of I which occurs rapidly and completely provided decarboxylation is avoided by adding I to the aqueous base. II was identified by reduction to isovaleric acid.

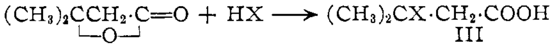


$$\begin{array}{l}(CH_3)_2C\text{—}CH_2\\ \qquad\quad | \qquad |\\ \qquad\quad O\text{—}C{=}O\end{array} + NaOH \longrightarrow \begin{array}{l}(CH_3)_2C\text{—}CH_2COONa\\ \qquad\quad |\\ \qquad\quad OH\end{array}$$

II

Polymers of I are formed similar to those for β-propiolactone[5] and are polyesters of low molecular weight. They are characterized by pyrolysis to β,β-dimethylacrylic acid, hydrolysis to β-hydroxyisovaleric acid and alcoholysis to β-hydroxyisovalerates.

Attempts to prepare β-bromoisovaleric acid from I and sodium bromide in water resulted in poor yields due to loss of most of I to carbon dioxide and isobutylene. However, fairly good yields of β-halogen acids III were obtained by addition of I to concentrated aqueous halogen acids.



$$(CH_3)_2\underbrace{CCH_2\cdot C{=}O}_{\text{—O—}} + HX \longrightarrow (CH_3)_2CX\cdot CH_2\cdot COOH$$

III

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[1] For paper XIII of this series, see THIS JOURNAL, **74**, 1323 (1952).

[2] β-Isovalerolactone was first prepared from β-bromoisovaleric acid by Sidney M. Hagman, Inaugural Dissertation, Lund University, 1924. Hydrolysis studies with acids and bases were reported also.

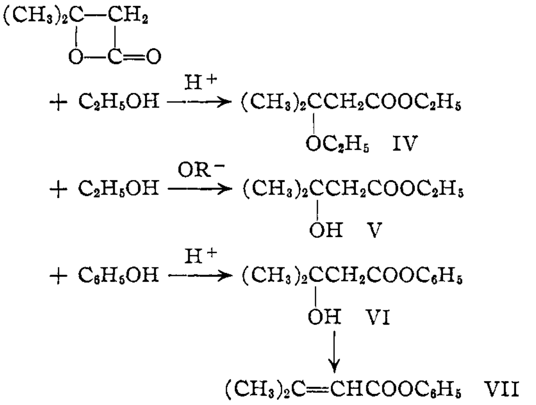
[3] Unpublished data from this Laboratory.

[4] P. D. Bartlett and Gilbert Small, Jr., THIS JOURNAL, **72**, 4868 (1950).

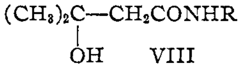
[5] T. L. Gresham, J. E. Jansen and F. W. Shaver, *ibid.*, **70**, 998 (1948).

This may be attributed to the stabilizing effect against decarboxylation by proton addition to the β-lactone ring.

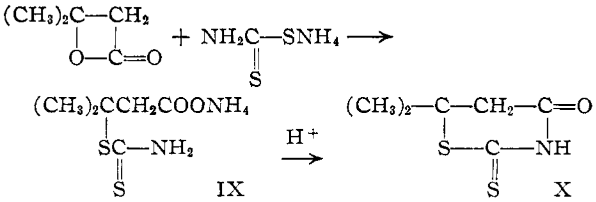
In boiling ethanol, decarboxylation of I was the principal reaction. However, at lower temperatures and in the presence of sulfuric acid a low yield of ethyl β-ethoxyisovalerate (IV) was isolated. This ester was most likely the result of esterification of alkoxy acid formed from I and alcohol and indicates that some beta attack occurred. With strong base catalysis I and alcohols formed β-hydroxyisovalerates (V) rapidly in high yield. With phenols and acid catalysis ring opening of I at the oxygen-carbonyl carbon bond occurred to give phenyl β-hydroxyisovalerate (VI) rapidly in good yield. This is similar to the observations with β-propiolactone.[6,7] The product VI was unstable so that only phenyl β,β-dimethylacrylate (VII) was isolated under the reaction conditions employed.



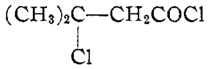
In acetonitrile, under conditions of amino acid formation with β-propiolactone and ammonia,[8] only slight reaction occurred with I and ammonia. In water, both ammonia and methylamine formed β-hydroxyisovaleramides (VIII) with I. These products were neutral, were distillable at reduced pressure and infrared absorption for both the hydroxyl and amide groups was evident. All of these properties would be inconsistent with amino acid or salt structures and verify the amide structure.


$$(CH_3)_2\underset{\displaystyle OH}{C}—CH_2CONHR$$
VIII

Attempts to titrate I with thiosulfate gave only small consumption of reagent and was thus of no value for analysis. Similarly poor reactions resulted with I and aqueous sodium hydrogen sulfide.[9] With ammonium dithiocarbamate in water I gives the β-dithiocarbamyl isovalerate (IX) in fair yield. Although the free acid was readily isolated in the unsubstituted series,[10] spontaneous ring closure occurred on acidification of IX to give the 2-thiono-4-keto-6,6-dimethyl-1,3-thiazane (X).



With thionyl chloride and I, fairly good yields of β,β-dimethylacrylyl chloride (XI) were isolated. This product is most probably the result of dehydrohalogenation of β-chloroisovaleryl chloride (XII),


$$(CH_3)_2\underset{\displaystyle Cl}{C}—CH_2COCl$$
XII

$(CH_3)_2C{=}CHCOCl$
XI

the expected product based on similar reactions with β-propiolactone.[11]

Experimental

β-Isovalerolactone (I).—Ketene[12] (0.81 mole per hour) was added below the surface of 300 g. of dry acetone containing 3 g. of boron trifluoride etherate. The solution was stirred while maintaining the temperature at −45° with a Dry Ice–acetone-bath. Boron trifluoride etherate (1 g.) was added at one-hour intervals and the operation continued for six hours. Dicyclohexylamine (14.4 g.) was added to neutralize the catalyst, the acetone removed by evaporation at reduced pressure and the product distilled, b.p. 49–51° at 10 mm., wt. 440 g. (90%), m.p. −26 to −26.5°, d^{20}_4 0.9898, n^{20}_D 1.4092; *MR* calcd. 24.77, found 24.99.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.06; sapn. equiv., 100. Found: C, 59.98; H, 8.10; sapn. equiv. (in ethanol), 99.8.

Addition of 20 g. of I to 250 ml. of distilled water gave immediate gas evolution. The gas was collected in a Dry Ice trap (wt. 9.5 g.), distilled through a soda lime tube to remove carbon dioxide and redistilled, b.p. −6°.

The boiling point, the bright yellow color with mercuric sulfate test paper and the complete similarity of the infrared curve with that for an authentic sample, identified this material as isobutylene. The presence of carbon dioxide in the water layer was shown by precipitation of barium carbonate.

β-Hydroxyisovaleric Acid (II).—I (50 g.) was added to a stirred solution of 25.3 g. of sodium hydroxide in 70 ml. of water. The solution was filtered from some insoluble material, 12 g. of Raney nickel catalyst added and II was reduced with hydrogen at 3000 p.s.i. and 180° for six hours. After filtration from catalyst, the solution was acidified and the resulting oil layer taken up in ether. The ether extracts were dried over anhydrous sodium sulfate, the ether evaporated and the residue distilled to give a fraction of isovaleric acid, b.p. 172–176°.

Anal. Calcd. for $C_5H_{10}O_2$: sapn. equiv., 102. Found: sapn. equiv., 101.

Polymerization.—Addition of two drops of concentrated sulfuric acid to 33 g. of I resulted in rapid heat evolution and formation of viscous oily polymer. Similar results were obtained by adding boron trifluoride etherate. Titration indicated a molecular weight of about 265.

Pyrolytic distillation of the above polymer at 15 mm. gave a liquid fraction of β,β-dimethylacrylic acid[13] boiling at 93–95° (19 mm.) on redistillation. After recrystallization from hexane the acid melted at 67–68°, wt. 22 g.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.06; neut. equiv., 100. Found: C, 60.09; H, 8.05; neut. equiv., 100.5.

A solution of 145 g. of polymer in 207 g. of absolute ethanol containing 2.5 g. of concentrated sulfuric acid was refluxed for 24 hours. The catalyst was neutralized by the addition of 5 g. of calcium carbonate, the solution filtered from salt, the excess alcohol evaporated at reduced pressure

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[6] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, W. L. Beears and M. G. Prendergast, THIS JOURNAL, **71**, 661 (1949).

[7] P. D. Bartlett and P. N. Rylander, *ibid.*, **73**, 4273 (1951).

[8] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert and F. T. Fiedorek, *ibid.*, **73**, 3168 (1951).

[9] T. L. Gresham, J. E. Jansen, F. W. Shaver and J. T. Gregory, *ibid.*, **70**, 1000 (1948).

[10] T. L. Gresham, J. E. Jansen and F. W. Shaver, *ibid.*, **70**, 1001 (1948).

[11] T. L. Gresham, J. E. Jansen and F. W. Shaver, *ibid.*, **72**, 72 (1950).

[12] J. R. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

[13] Ph. Barbier and G. Leser, *Bull. soc. chim.*, [3] **33**, 815 (1905).

and the residue distilled to give a fraction of ethyl β-hydroxyisovalerate, b.p. 70–72° at 8 mm., wt. 27 g., d^{25}_4 0.9740, $n^{25}\text{D}$ 1.4183.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.76. Found: C, 57.51; H, 9.67.

β,β-Dimethylacrylic Acid.—An alternate procedure[14] consisted of adding 20 g. of I to 3 g. of concentrated sulfuric acid. On cooling the solid acid was extracted with and recrystallized from hexane, m.p. 68–69°, wt. 16 g. (80%). A mixture melting point with an authentic sample of β,β-dimethylacrylic acid was not depressed.

β-Halogenoisovaleric Acids (III).—A solution of 10 g. of I in 50 g. of concentrated hydrochloric acid was allowed to stand overnight. The crystals of β-chloroisovaleric acid[15] which had separated were isolated by filtration, dried and recrystallized from hexane, m.p. 56–57°, wt. 3 g.

Anal. Calcd. for $C_5H_9O_2Cl$: Cl, 26.0. Found: Cl, 25.95.

A similar experiment but adding 25 g. of I to 84.5 g. of 48% hydrobromic acid in water gave β-bromoisovaleric acid,[16] m.p. 73–74°, wt. 29 g.

Anal. Calcd. for $C_5H_9O_2Br$: C, 33.17; H, 5.01; Br, 44.14. Found: C, 33.60; H, 5.23; Br, 43.6.

A third experiment but adding 25 g. of I to 114 g. of concentrated hydrogen iodide (64 g. of HI) gave β-iodoisovaleric acid,[17] m.p. 82–83°, wt. 14 g.

Anal. Calcd. for $C_5H_9O_2I$: C, 26.32; H, 3.95. Found: C, 26.59; H, 4.09.

Ethyl β-Ethoxyisovalerate (IV).—A solution of 100 g. (1 mole) of I in 276 g. (6 moles) of anhydrous ethanol containing 1 g. of concentrated sulfuric acid was stirred for two hours at room temperature and heated two hours at 80°. The catalyst was neutralized by addition of 2 g. of calcium carbonate, the solution filtered from salt and distilled at reduced pressure. After removal of the alcohol a fraction was collected at 42–44° at 45 mm., wt. 35 g.

Anal. Calcd. for $C_9H_{18}O_3$: sapn. equiv., 170. Found: sapn. equiv., 174.

Ethyl β-Hydroxyisovalerate[18] (V).—Addition of 50 g. of I dropwise (30 min.) to a stirred solution of 0.5 g. of sodium in 138 g. of absolute ethanol while maintaining the temperature at 17° with external cooling gave a clear solution. After standing for an additional hour the solution was neutralized with 2.5 g. of concentrated hydrochloric acid, filtered from salt and distilled at reduced pressure. The residue after removal of the excess alcohol distilled at 70–72° at 8 mm., wt. 62 g., d^{25}_4 0.9740, $n^{25}\text{D}$ 1.4183.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.76. Found: C, 57.51; H, 9.67.

Phenyl β,β-Dimethylacrylate (VII).—Seventy-five grams (0.75 mole of I) was added dropwise (30 min.) to 352 g. (3.75 moles) of phenol containing 0.5 g. of concentrated sulfuric acid while stirring and maintaining the temperature at 50° with heating. After an additional hour the catalyst was neutralized with 0.96 g. of sodium phenoxide, the solution filtered from salt and distilled at reduced pressure. After removal of the excess phenol the residue (57 g.) was taken up in ether and the solution extracted three times with saturated sodium bicarbonate. Acidification of the extract gave only a trace of oil. The ether solution was washed with water, dried over anhydrous magnesium sulfate, the ether evaporated and the residue distilled giving a main fraction, b.p. 55–56.5° at 0.1 mm., wt. 22.5 g.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.06; H, 6.87. Found: C, 75.33; H, 7.11.

β-Hydroxyisovaleramide (VIII).—Twenty grams (0.2 mole) of I was added (15 min.) to 125 g. of 28% ammonium hydroxide while stirring and maintaining the temperature at 20° with external cooling. After standing overnight the solution was evaporated to dryness under vacuum. The solid residue (21 g.) was recrystallized from acetone from which it separated in rectangular plates, m.p. 92–94°. The product distilled at 132° at 2 mm.

Anal. Calcd. for $C_5H_{11}O_2N$: N, 11.97. Found: N, 11.87.

A similar experiment but adding 30 g. of I to 186 g. of 25% methylamine in water gave 21.5 g. of N-methyl-β-hydroxyisovaleramide, b.p. 80–82° at 0.5 mm.

Anal. Calcd. for $C_6H_{13}O_2N$: N, 10.69. Found: N, 10.48.

2-Thiono-4-keto-6,6-dimethyl-1,3-thiazane (X).—Twenty-five grams (0.25 mole) of I was added (20 min.) to 55 ml. (0.25 mole) of 50% aqueous ammonium dithiocarbamate while stirring and maintaining the temperature at 0° with external cooling. After an additional two hours at 0° the solution was acidified with 25 ml. of concentrated hydrochloric acid. The oil layer which separated crystallized on standing. Recrystallization of the solid from alcohol-water gave yellow needles, m.p. 140.5–141.5°, wt. 15 g.

Anal. Calcd. for $C_6H_9ONS_2$: C, 41.14; H, 5.14; N, 8.00; neut. equiv., 175. Found: C, 41.26; H, 5.18; N, 7.96; neut. equiv., 175.3.

β,β-Dimethylacrylyl Chloride (XI).[19]—I (50 g., 0.5 mole) was added dropwise (30 min.) to 88 g. (0.74 mole) of thionyl chloride (Eastman Kodak Company White Label) while stirring and maintaining the temperature at 30–35° with external cooling. Concentrated sulfuric acid (1.5 g.) was then added and the solution heated to reflux for three hours to remove hydrogen chloride. Distillation through a 1″ × 12″ column packed with glass helices gave a fraction of β,β-dimethylacrylyl chloride, b.p. 90–92° at 95 mm., wt. 36.1 g. (61%), $n^{25}\text{D}$ 1.4707, d^{25}_4 1.0625.

Addition of the above liquid to an equal volume of water gave a solid which after recrystallization from hexane, melted at 69°. A mixture melting point with an authentic sample of β,β-dimethylacrylic acid was not depressed.

Brecksville, Ohio

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[14] W. L. Beears and J. E. Jansen, U. S. Patent 2,623,067 (1952).

[15] C. Montemartini, *Gazz. chim. ital.*, **28**, II, 305 (1898).

[16] K. Auwers, *Ber.*, **28**, 1133 (1895).

[17] A. Schirokoff, *J. prakt. Chem.*, [2] **23**, 285 (1881).

[18] G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, **127**, 620 (1925).

[19] H. Staudinger and E. Ott, *Ber.*, **44**, 1636 (1911).