

ated at the aspirator. Following the introduction of oxygen at a pressure of about two atmospheres, the reaction was initiated when the sealed vessel was broken by vigorous mechanical shaking. Agitation was continued at a rate of 100-150 oscillations per minute until the desired amount of oxygen had been absorbed or until uptake was immeasurably slow. The reaction vessel and oxygen tank had a volume of 3.6 l. corresponding to a pressure drop of 9.0 lb. per 0.1 mole of oxygen consumed. Table I gives the material data on substances oxidized.

Benzylacetophenone (I).—In expt. 1 (Table I), I, m.p. 71-71.5° (obtained from hydrogenation of benzalacetophenone using Adams catalyst), absorbed 4.5 lb. (0.05 mole) of oxygen in the first 2.5 min. and an additional 5.1 lb. (0.056 mole) in the following 6 hr. Concentration of the reaction mixture to dryness gave a residue which, after being washed with ether and acidified, yielded 11.9 g. of acid, m.p. 110-115°. Fractional crystallization from hexane and sublimation separated the crude material into two fractions: 4.32 g. (35% of the theoretical based on two equivalents) of benzoic acid, m.p. 122-122.5°, and 1.56 g. (13% yield) of phenylbenzylglycolic acid, m.p. 166.5-167° (reported¹⁵ m.p. 165-166°).

Anal. Calcd. for C₁₅H₁₄O₃: C, 74.4; H, 5.8; neut. equiv., 242.3. Found: C, 74.3; H, 5.6; neut. equiv., 240.0.

TABLE I

Expt.	Substance	G.	Mole	$\frac{t}{\text{KOC-}} \frac{t}{\text{H}_2}$ mole	$\frac{t}{\text{HOC-}} \frac{t}{\text{H}_2}$ cc.
1	Benzylacetophenone (I)	10.5	0.05	0.18	300
2	Phenylacetaldehyde (II)	9.44	.08	.24	300
3	Phenylacetaldehyde (II)	24.0	.20	.20	150
4	Benzyl alcohol	10.8	.10	.11	300
5	Desoxybenzoin (IV)	9.8	.05	.10	85
6	Cyclohexanone	20.6	.20	.20	600
7	<i>dl</i> -Camphor	15.2	.10	.20	200
8	<i>d</i> -Camphor	7.6	.05	.06	100
9	Acetophenone	6.0	.05	.17	300
10	Propiophenone	6.7	.05	.17	300
11	Isobutyrophenone	7.4	.05	.05	300
12	Dypnone	11.1	.05	.20	300
13	Benzalacetophenone	10.4	.05	.20	200
14	Benzalpinacolone	9.4	.05	.20	300
15	Ethyl phenylacetate	8.2	.05	.11	300
16	<i>t</i> -Butyl β -phenylpropionate	9.5	.046	.20	300
17	Ethyl γ -phenylbutyrate	9.83	.051	.23	250
18	<i>t</i> -Butyl cinnamate	10.0	.05	.20	300
19	Ethyl benzoylacetate	9.6	.08	.08	300
20	5,5-Dimethyldihydroresorcinol	14.0	.10	.10	300
21	2,5,5-Trimethyldihydroresorcinol	6.9	.05	.05	300
22	Diethyl malonate	8.0	.05	.05	300
23	Diethyl phenylmalonate	23.6	.10	.10	300

Phenylbenzylglycolic acid (0.7 g.) was further characterized by oxidation with 0.29 g. of potassium dichromate in a few drops of water and acetic acid. After 2 hr. at room temperature, the solution was neutralized with solid sodium carbonate and extracted with ether. Two crystallizations of the concentrated extract from 95% ethanol gave 0.21 g. of desoxybenzoin, m.p. 56-57°, which gave no depression in m.p. when mixed with an authentic sample.

Phenylacetaldehyde (II).—II in expt. 2 (Table I) absorbed 8.9 lb. (0.099 mole) of oxygen in the first 15 min. and

an additional 5.1 lb. (0.056 mole) in the next 4.3 hr. The filtered precipitate was dissolved in water and on acidification gave 10.5 g. of crude benzoic acid, m.p. 119-120°, which was recrystallized from water, giving 6.64 g. of pure benzoic acid, m.p. 122-122.5° (68% yield).

In shortening the total reaction time to 20 min., II in expt. 3 (Table I) absorbed 12.5 lb. (0.4 mole) of oxygen, the temperature rising to 75°. The solution was extracted once with saturated potassium carbonate solution, the alcohol layer was separated by centrifuging and treated with saturated, aqueous sodium bisulfite, additional solid sodium bisulfite being added to maintain saturation. After remaining at 4° for two days, the solution deposited 8.06 g. of a sodium bisulfite addition product (19% yield) which was decomposed with 10% aqueous sodium carbonate. The ethereal extract was added to an alcoholic solution of 6.0 g. of 2,4-dinitrophenylhydrazine. The ether having been evaporated, 6 cc. of concentrated hydrochloric acid was added and the solution refluxed for 30 min. Upon cooling, the solution deposited 4.9 g. of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 180-198°, which on recrystallization from 800 cc. of 95% ethanol and chloroform gave 1.99 g. of pure material, m.p. 236-237°, showing no m.p. depression on admixture with an authentic sample.

Benzaldehyde (III).—A 0.40 *M* solution of III (10 cc., 0.1 mole) in anhydrous *t*-butyl alcohol (250 cc.) was found to be 8×10^{-5} *M* in perbenzoic acid by iodometric titration with 0.0966 *M* sodium thiosulfate. After being shaken for 4 hr. under *ca.* 30 lb. of oxygen the solution had absorbed 0.025 mole of oxygen and was 0.0022 *M* in perbenzoic acid. The solution was treated with 0.4 mole of potassium *t*-butoxide in 100 cc. of anhydrous *t*-butyl alcohol and shaken with oxygen for 15 hr., 0.1 mole of oxygen being consumed. Titration of a 2-cc. aliquot showed that 0.09 mole of base had been neutralized in the reaction. Benzoic acid (10.51 g.) was isolated in 82% of the theoretical yield.

Benzyl Alcohol.—In expt. 4 (Table I) benzyl alcohol absorbed 6.0 lb. (0.066 mole) in 9 hr., affording 8.33 g. (66% yield) of benzoic acid, m.p. 119-122.5° without recrystallization.

Desoxybenzoin (IV).—In expt. 5 (Table I) IV (prepared by the method of Sudborough¹⁶) reacted with 0.076 mole of oxygen in 2.5 min., the temperature reaching 70°. The precipitate yielded 9.0 g. of benzoic acid (74% yield), m.p. 121-122° without recrystallization.

Oxygen at atmospheric pressure was bubbled into 200 cc. of anhydrous *t*-butyl alcohol containing 0.2 mole of potassium *t*-butoxide for one hour. IV (20 g., 0.1 mole) was added and the treatment with oxygen was continued for 1.5 hr. The filtered precipitate was washed with ether and acidified with 2 *N* hydrochloric acid, giving 15.5 g. of material, m.p. 146-149°. The latter was partially dissolved in 500 cc. of boiling water, treated with sodium carbonate and filtered from 1.95 g. of material, m.p. 200-201.5°, which was not investigated further. Acidification of the alkaline solution precipitated 7.37 g. of benzoic acid, m.p. 147° (no depression with an authentic sample). Ether extraction of the aqueous mother liquor afforded 2.29 g. of crude acid. From the alcoholic filtrate of the reaction mixture additional benzoic acid (1.1 g.) was obtained, bringing the total yield to 60%.

Cyclohexanone.—In 4 min. the temperature rose to 83° and 0.18 mole of oxygen was absorbed in expt. 6 (Table I) when cyclohexanone was oxidized. Removal of most of the solvent by distillation left a yellow precipitate which was washed with anhydrous ether and added to a solution of 100 cc. of anhydrous ethanol and 45 cc. of ethyl orthoformate (0.27 mole). Hydrogen chloride was bubbled through the cooled (-10°) solution for 20 min. After standing for 3 hr., the solution was neutralized with excess anhydrous sodium bicarbonate, diluted with ether and washed successively with cooled, saturated sodium chloride. Concentration of the dried, ethereal solution left a viscous residue which gave, after flash distillation, 4 g. of an orange-yellow liquid, presumably ϵ -(diethoxymethoxy)-hexanolactone (VII, 8.7% yield). A portion of VII which had been evaporatively distilled four times had the following physical constants: $n_{D}^{22.5}$ 1.4319, $d_{4}^{22.5}$ 1.0471; M_D calcd. 57.38, found 57.49.

Anal. Calcd. for C₁₁H₂₀O₆: C, 56.9; H, 8.7; C₂H₅O, 38.8. Found: C, 56.6; H, 8.6; C₂H₅O, 38.8.

(15) O. Widman, *Ber.*, **49**, 477 (1916).

(16) J. J. Sudborough, *J. Chem. Soc.*, **71**, 218 (1897).

A small amount of VII treated with concentrated nitric acid gave adipic acid, m.p. 149–150°, identical with an authentic sample.

The solid yellow residue obtained as above from the oxidation of 0.1 mole of cyclohexanone was washed thoroughly with anhydrous ether, suspended in 80 cc. of anhydrous ethanol, cooled in a salt-ice-bath and treated with hydrogen chloride gas for 20 min. By proceeding as above, a viscous material was obtained from which vacuum distillation separated 0.6 g. and evaporative distillation afforded an additional 1.2 g. (total yield 11%) of a colorless liquid, presumed to be ϵ -ethoxyhexanolactone (VI), b.p. 76–79° (3 mm.). Two evaporative distillations gave purer VI: n_D^{20} 1.4440, d_4^{20} 1.0457; M_D calcd. 40.24, found 40.18.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.3; H, 8.3.

A small amount of VI treated with concentrated nitric acid gave adipic acid, m.p. 149–150°.

dl-Camphor.—In expt. 7 (Table I), oxygen was bubbled through the reaction mixture for 4 hr. After the addition of water, the aqueous layer was extracted with ether, acidified and again extracted with ether. Concentration of this ether extract gave 2 g. (10% yield) of crude camphoric acid, m.p. 197–198°; after recrystallization from acetic acid, m.p. 199–200° (reported¹⁷ m.p. 202–203°).

d-Camphor.—In expt. 8 (Table I) *d*-camphor ($[\alpha]_D^{20} +43^\circ$) absorbed 0.012 mole of oxygen in 7 hr. The reaction product, obtained by removing the solvent, was dissolved in water, extracted with ether, acidified and extracted again with ether giving 0.53 g. (5.3% yield) of *d*-camphoric acid; after recrystallization from acetic acid, m.p. 184–185° (reported¹⁸ m.p. 187°).

Acetophenone.—Acetophenone, in expt. 9 (Table I), was oxidized slowly, 0.062 mole being consumed in 2.5 hr. The aqueous solution of the concentrated reaction mixture was extracted with ether, and acidified, giving 3.8 g. of benzoic acid, m.p. 115–121°, and an additional 0.5 g. by ether extraction (total yield 68%). Recrystallization from *n*-heptane gave 3.44 g. of benzoic acid, m.p. 120–122°.

Propiophenone.—In expt. 10 (Table I) propiophenone consumed 0.061 mole of oxygen in 10 min., affording 3.85 g. of benzoic acid, m.p. 120–121° (63% yield).

Isobutyrophenone.—In expt. 11 (Table I), isobutyrophenone absorbed 0.063 mole of oxygen in 7 min. to yield 6.6 g. of dark colored acid, m.p. 116–121°, a *n*-heptane solution of which, after filtration from 0.29 g. of unidentified material, deposited 4.58 g. of benzoic acid, m.p. 121–122.5° (75% yield).

Dyponone.—In expt. 12 (Table I) dyponone (prepared by the method of Kohler¹⁹) absorbed 0.11 mole of oxygen in 12 min. The concentrated reaction mixture was dissolved in water and thoroughly extracted with ether giving an undistillable dark brown tar. Acidification and ether extraction of the aqueous solution gave a solid residue which upon sublimation yielded 4.0 g. of benzoic acid, m.p. 119–121° (33% based on two equivalents).

Benzalacetophenone.—In expt. 13 (Table I) benzalacetophenone, m.p. 56–57°, absorbed 9.3 lb. (0.103 mole) of oxygen in 18.5 hr. The reaction mixture was concentrated to about 50 cc. and diluted with water dropwise until the precipitate had dissolved. The ethereal extract was washed several times with water, the aqueous washings being combined with the main aqueous phase. Acidification of the aqueous solution gave 1.16 g. of benzoic acid, m.p. 119–122° (75% based on two equivalents). Concentration of the ethereal layer afforded 0.17 g. of material, m.p. 218–220°, not further identified.

Benzalpinacolone.—Benzalpinacolone²⁰ (expt. 14, Table I) absorbed 5.4 lb. (0.06 mole) of oxygen in 42 hr. at 27° and 6.1 lb. (0.066 mole) in 4 hr. at 60°. The latter reaction mixture, after concentration, was diluted with ether, and extracted with water. Distillation of the dried, ethereal extract of the combined, acidified washings gave 2.8 g. of trimethylacetic acid, m.p. 33–35° (55% yield).

Ethyl Phenylacetate.—Ethyl phenylacetate (expt. 15, Table I) absorbed 0.11 mole of oxygen in 8.5 hr., affording 3.5 g. of benzoic acid (56% yield).

(17) O. Aschan, *Ann.*, **316**, 196 (1901).

(18) O. Aschan, *Ber.*, **27**, 2001 (1894).

(19) E. P. Kohler, *Am. Chem. J.*, **31**, 658 (1904).

(20) Prepared by the method described in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 81.

Preparation and Oxidation of *t*-Butyl β -Phenylpropionate.—*t*-Butyl β -phenylpropionate, b.p. 86–88° at 1.5 mm., n_D^{20} 1.4801, was prepared in 55% of the theoretical yield by the method of Abramovitch, *et al.*²¹

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 75.7; H, 8.7. Found: C, 75.8; H, 8.8.

In expt. 16 (Table I) this ester absorbed 0.01 mole of oxygen in 43 hr. Bubbling carbon dioxide into the reaction mixture precipitated a thick paste which was dissolved in water. The solution was brought to pH 8 by treating with solid carbon dioxide and extracting with ether. Acidification and ether extraction of the aqueous phase gave dark brown material which was sublimed to yield 0.16 g. of β -phenylpropionic acid, m.p. 46–47°. The dried ethereal extract was distilled giving 3.66 g. of *t*-butyl β -phenylpropionate, b.p. 80–85° at 1 mm. (39% recovery). No products of oxidation could be isolated.

Ethyl γ -Phenylbutyrate.—Ethyl γ -phenylbutyrate, prepared by the method of von Braun,²² in expt. 17 (Table I), reacted with 7.3 lb. (0.081 mole) of oxygen in 23 hr. The residue obtained from concentration of the reaction mixture, upon acidification with concentrated hydrochloric acid, gave 3.83 g. of γ -phenylbutyric acid, m.p. 50–51°, mixed m.p. 50–51°, representing a recovery of 41.7% of the starting material.

***t*-Butyl Cinnamate.**—In expt. 18 (Table I) *t*-butyl cinnamate (prepared by the method of Abramovitch, *et al.*²¹) failed to react with oxygen over a period of 5.5 hr. There was recovered 6.0 g. (54%) of the ester and 2.55 g. of cinnamic acid, m.p. 132–133°, representing a total recovery of 88% of the starting material.

Ethyl Benzoylacetate.—In expt. 19 (Table I), ethyl benzoylacetate gave a precipitate and failed to absorb oxygen. The precipitated potassium salt was removed by centrifugation, dissolved in 250 cc. of 2 *N* potassium hydroxide and shaken under *ca.* two atmospheres of oxygen. No oxygen was absorbed.

5,5-Dimethyldihydroresorcinol.—In expt. 20 (Table I), a homogeneous solution absorbed no oxygen in 17 hr. Even at 60° for 4 hr. no oxygen was taken up, 5,5-dimethyldihydroresorcinol being recovered in 87% yield.

2,5,5-Trimethyldihydroresorcinol.—In expt. 21 (Table I), a homogeneous solution of 2,5,5-trimethyldihydroresorcinol (prepared by the method of Desai²³) absorbed no oxygen.

Diethyl Malonate.—Neither a heterogeneous mixture (expt. 22, Table I) of diethyl malonate nor the homogeneous solution of 8.0 g. (0.05 mole) of diethyl malonate in 300 cc. of 2 *N* aqueous potassium hydroxide absorbed any oxygen.

Diethyl Phenylmalonate.—In expt. 23 (Table I), diethyl phenylmalonate consumed 0.1 mole of oxygen in 1 hr. After concentration to approximately 100 cc. and addition of ether, the reaction mixture was washed with water until neutral. The aqueous washings were combined, acidified and extracted with ether to give, after recrystallization from *n*-hexane, 1.63 g. of benzoic acid, m.p. 119–120°. The dried ethereal extract was distilled giving three fractions: (a) 0.77 g., b.p. below 50° at 0.2 mm., n_D^{20} 1.4982; (b) 3.46 g., b.p. 82° at 0.2 mm., n_D^{20} 1.5011; and (c) 5.61 g., b.p. 82–112° at 0.3 mm., n_D^{20} 1.4880.

Hydrolysis with concentrated hydrochloric acid of 0.39 g. of fraction (a) gave 0.02 g. of benzoic acid, m.p. 120–121°. Evaporative distillation of 1.96 g. of fraction (b) gave 0.14 g. of material evaporating at room temperature at 0.05 mm., and 0.94 g. of ethyl phenylglyoxylate evaporating at 45° at 0.05 mm. (see analysis) leaving a residue of 0.26 g. of higher boiling material.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.7. Found: C, 67.1; H, 5.4.

The 2,4-dinitrophenylhydrazone of fraction (b) was prepared from 0.33 g. of un-redistilled liquid, giving 0.44 g. of yellow-orange needles, m.p. 148–176°. The derivative, recrystallized first from ethanol and then from benzene, m.p. 183–184.8° dec., is apparently the 2,4-dinitrophenylhydrazone of *t*-butyl phenylglyoxylate.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 56.0; H, 4.7; N, 14.5. Found: C, 55.8; H, 4.5; N, 14.7.

(21) B. Abramovitch, J. C. Shivers, B. E. Hudson and C. R. Hauser, *THIS JOURNAL*, **65**, 986 (1943).

(22) J. v. Braun, *Ber.*, **44**, 2867 (1911).

(23) R. D. Desai, *J. Chem. Soc.*, 1079 (1932).

Evaporative distillation of 2.1 g. of fraction c gave 1.5 g. of material distilling at 45° at 0.05 mm., n_D^{25} 1.4952, d_4^{25} 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 Böttler²⁴ 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 Kohler²³ by instantly treating a moist ethereal solution of the decomposed Grignard addition product of ethylmagnesium bromide and benzaldehyde with air. Kohler reported the isolation of two isomers, m.p. 166° and m.p. 109° (no decomposition), neither of which liberated iodine

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

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 ethyldeoxybenzoin, m.p. 56–57°, reported m.p. 58°. ²⁵

Anal. Calcd. for $C_{18}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.6; H, 7.1.

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

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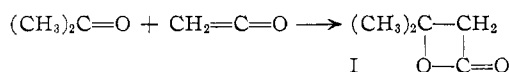
β -Propiolactone. XIV.¹ β -Isovalerolactone

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

RECEIVED SEPTEMBER 14, 1953

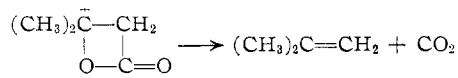
The reactions of β -isovalerolactone are similar to those of β -propiolactone except for a rapid loss of carbon dioxide in polar solvents and a greater difficulty of substitution at the β -tertiary carbon atom. Polymerization, hydrolysis and reactions of β -isovalerolactone with halogen acids, alcohols, 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 -isovalerolactone² (I) was prepared from ketene and acetone.



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

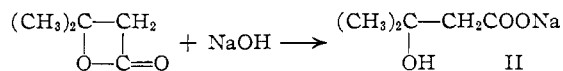
In water at room temperature, I decomposes rapidly to carbon dioxide and isobutylene to the near exclusion of hydrolysis. This is probably due to a tendency for ionization at the tertiary carbon–oxygen bond with subsequent shift of electrons and expulsion of carbon dioxide occurring more rapidly



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

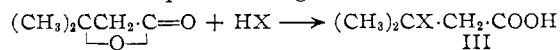
unsubstituted β -lactone. Reactions due to attack at the carbonyl group with ordinary ester type ring opening occur in a normal manner.

The very rapid reaction of hydroxyl ion with β -propiolactone is attributed⁴ 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.



Polymers of I are formed similar to those for β -propiolactone⁵ 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.



(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).