shaken thoroughly to ensure homogeneity of the solution. By making up solutions in the manner outlined, the resultant sucrose concentration of the reaction mixture was 10%.

At recorded time intervals, twenty-five cc. of the reaction mixtures were delivered from a pipet into bottles containing saturated alkali in sufficient[14] amount to stop the hydrolysis. After allowing about five to fifteen minutes for mutarotation, the rotation of the solutions in the bottles was determined.

The buffered solutions were prepared by mixing, in definite proportions by volume *M*/10 citric acid and *M*/5 disodium phosphate solutions, the actual proportions depending upon the *p*H desired. It is obvious that the salt concentrations varied with the *p*H (0.12 *M* at *p*H 3 and 0.18 *M* at *p*H 6.5), but since control hydrolyses were always conducted under the same conditions of hydrogen-ion concentration, temperature, etc., and since only relative differences of activity were significant, this factor was disregarded.

If protein was to be present in the reaction mixture, it was usually added to the sucrose solution before adjusting the latter to standard volume. However, it was shown that no difference, within experimental error, could be detected if protein was added first to the enzyme solution or to the sucrose solution.

Concentrations of protein greater than 50 mg. in 225 cc. were deliberately avoided because of the increased viscosity, and the tendency to foam made the drawing of samples by means of a pipet difficult, if air bubbles were to be excluded from the sample when drawn up into the pipet.

The change in the hydrogen-ion concentration of the buffered sucrose solutions when 10 to 50 mg. of protein were added, was at most one or two hundredths of a *p*H unit, so that the effect on the rate of reaction of such a difference is within experimental error. Finally the *p*H, as measured by a hydrogen electrode, of the reaction mixture was demonstrated to remain unaltered during the course of hydrolysis, by making such determinations before and after hydrolysis of the sucrose.

Before using undenatured protein, a solution of the protein was always examined to determine the presence of denatured protein. If more than a faint opalescence was observed in the solution, the protein was recrystallized or an entirely new quantity prepared.

## Summary

1. Undenatured egg albumin, edestin, pepsin, globin and serum accelerate the activity of purified yeast invertase preparations at *p*H 3 but not at 4.5.

2. In the undenatured state edestin does not affect the activity of invertase at the *p*H optimum of yeast invertase or at the *p*H values 5.88 and 6.51.

3. Gum arabic, gelatin, glycylglycine and tryptophan do not affect the activity of purified invertase preparations at *p*H 3.

4. Undenatured serum and edestin did not affect the activity of several crude invertase solutions at *p*H 3.

5. Denatured edestin, pepsin, egg albumin or globin do not affect the activity of highly purified invertase preparations at *p*H 3.

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(14) When citrate–phosphate buffer solutions at *p*H 3 were used it was necessary to add five drops of saturated sodium hydroxide, while at *p*H 4.6, only three drops were required. However, since all samples removed from the reaction mixture were treated in the same way, for any given *p*H it is clear that the reaction rates were not affected.

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[CONTRIBUTION FROM STANDARD ALCOHOL CO.]

# The Reaction of Propylene, Pentene-1 and Pentene-2 with Sulfuric Acid

BY BENJAMIN T. BROOKS

Kharasch and his co-workers have indicated that the presence of organic peroxides influences the addition of hydrogen bromide to olefins of the type $RCH{=}CH_2$, peroxides favoring the formation of primary halides, and in the case of propylene reported the formation of large proportions of normal propyl bromide.[1] Ingold and Ramsden[2] reported the formation of 24.8% normal propyl bromide in propane solution and 2.8% in a water solution. Sherrill, Mayer and Walter[3] have recently shown that pentene-1 and heptene-1, on treating with hydrogen bromide in glacial acetic acid, hexane or carbon tetrachloride, give exclusively 1-bromopentane and 1-bromoheptane, respectively, and that 48% aqueous hydrobromic acid gave only the 2-bromo derivatives from these olefins. Ingold and Ramsden[2] have also shown that in water solution only 2-bromopentane is formed from pentene-1.

In view of these facts and since the reaction of these and other olefins with sulfuric acid, followed by hydrolysis to alcohols, is carried out industrially on a large scale, it was of interest to compare the manner of the addition of sulfuric acid to ole-

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(1) Kharasch, McNab and Mayo, THIS JOURNAL, **55**, 2531 (1933).

(2) Ingold and Ramsden, *J. Chem. Soc.*, 2752 (1931).

(3) Sherrill, Mayer and Walter, THIS JOURNAL, **56**, 926 (1934).

fins of the type $RCH{=}CH_2$, with the behavior of the halogen acids, as noted above.

Although the reaction of sulfuric acid and propylene is not carried out under anhydrous conditions, 90–92% sulfuric acid being used, the reaction is carried out in the presence of a solvent oil. As more fully described later, no normal propyl alcohol was found among the reaction products.

In addition to isopropyl alcohol, a very small proportion, less than 0.2%, of a hexyl alcohol is formed, which was isolated and identified as 4-methylpentanol-2, indicating that the constitution of the hexene formed by polymerization of the propylene is 4-methylpentene-1, $(CH_3)_2CH{-}CH_2CH{=}CH_2$.

Pentene-1, which is probably present in only small proportions in the amylene fraction of cracked naphtha, was prepared by the reaction of allyl bromide on ethylmagnesium bromide, according to the method described by the writer with I. W. Humphrey.[4] On treating pentene-1 with 85% sulfuric acid containing about 1% hydrogen peroxide, and benzoyl peroxide, pentanol-2 exclusively was formed.

Pentene-2 treated with 80% sulfuric acid and hydrolyzing gave a mixture of approximately 70 parts pentanol-2 and 30 parts of pentanol-3. The latter alcohol was also isolated from commercial secondary amyl alcohol made from the amylene fraction of cracked naphtha. The isomeric alcohols were separated by repeated fractional distillation and in each case the identifications were made by means of the $\alpha$-naphthyl urethans.

The addition of hydrogen bromide to pentene-2 has been critically reviewed by Lauer and Stodola,[5] who used the melting points of the anilides instead of the refractive indices for determining the relative amounts of the 2- and 3-bromopentanes formed. They found that pentene-2 made from 3-bromopentane and also from $\alpha$-ethyl-$\beta$-bromobutyric acid gave nearly equal proportions of 2-bromo and 3-bromopentane, and pointed out that these results are not in accord with the theory of stable and unstable electromeric forms of pentene-2 suggested by Kharasch and Darkis.[6] Lauer and Stodola found that the physical properties of the pentene-2 made from the butyric acid derivative agreed with the physical properties of the pentene-2 made by van Risseghem[7] and regard this pentene-2 as the more stable of the geometrical isomers. They do not confirm the results of Sherrill and her co-workers,[8] which indicated, by the refractive index method of analysis, that pentene-2 made by decomposition of 3-bromopentane gave 93–95% 3-bromopentane, and that made from 2-bromopentane gave 93–95% 2-bromopentane. Norris and Reuter[9] found no evidence of the formation of 3-chloropentane on adding hydrogen chloride to pentene-2.

It is not possible to use anhydrous or 100% sulfuric acid in the reaction with pentenes except to get polymers and other side reactions.

The pentene-2 used in the present work was prepared by heating commercial secondary amyl alcohol with 50% sulfuric acid and fractionating the resulting pentene. Sherrill, Baldwin and Haas[8] made pentene-2 in this way and the physical properties of this pentene-2 agree closely with the values recorded by Norris and Reuter, by van Risseghem and by Lauer and Stodola for the higher boiling one, regarded by Lauer and Stodola as the more stable geometrical isomer. It is highly probable that both pentanol-2 and pentanol-3 would yield the same pentene-2, boiling at 36.4°, by decomposition in sulfuric acid solutions.

Pentanol-2 boils at 119.2° and pentanol-3 at 115–116° and repeated fractional distillation gives only an approximation of the proportions of the two alcohols in the mixture. However, the results show approximately 35% pentanol-3 and 65% pentanol-2 in the product from pentene-2. The commercial alcohol, made from an amylene fraction derived from cracked naphtha and containing also pentene-1, showed approximately 20% pentanol-3 and 80% pentanol-2.

### The Reaction Products of Propylene

In the manufacture of isopropyl alcohol, the sulfuric acid reaction product is distilled with steam. The crude isopropyl alcohol is then redistilled continuously through a column and a high boiling alcohol fraction is obtained. Four gallons of this higher boiling alcohol fraction were examined for normal propyl alcohol. After drying by caustic soda and removal of 20% isopropyl alcohol by fractional distillation, evidence of normal propyl alcohol was sought in the fraction distilling at 97–98.5°. Since the acetates of *n*-propyl and *s*-butyl alcohols boil at 100.8 and 111.5–112°, respectively, 600 g. of the alcohol fraction was acetylated and the product distilled through a 50 cm. Widmer column. The product proved to be secondary butyl acetate exclusively.

A higher boiling alcohol fraction, 220 ml., distilling at 130–142° was collected. On distilling through a 50 cm. Widmer column, the product was concentrated in a fraction distilling at 136–138°. The $\alpha$-naphthyl urethan, after recrystallizing from petroleum ether, melted at 87–88°. Levene and Walti[10] give 86–89° as the melting point of the $\alpha$-naphthyl urethan of 4-methylpentanol-2. Hexyl

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[4] Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918).

[5] Lauer and Stodola, *ibid.*, **56**, 1215 (1934).

[6] Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

[7] Van Risseghem, *Bull. soc. chim. Belg.*, **28**, 53, 187, 288 (1914).

[8] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929).

[9] Norris and Reuter, *ibid.*, **49**, 2630 (1927).

[10] Levene and Walti, *J. Biol. Chem.*, **94**, 367 (1931).

alcohol made by the action of sulfuric acid on cracked petroleum hexene fraction is mainly hexanol-2, the fraction distilling at 138–139° giving an α-naphthyl urethan melting, not sharply, at 58–62°. Levene and Haller[11] have recorded 61–65° as the melting point of the α-naphthyl urethan of *d*-hexanol-2.

### Reaction of Pentene-1 with Sulfuric Acid

Pentene-1 was prepared by the action of allyl bromide on ethylmagnesium bromide, ether being removed from the pentene by treating with 70% sulfuric acid below 20°. The pentene, 80 g., b. p. 30–30.5°, was treated with 130 g. of sulfuric acid 84%, containing 3 ml. of Merck "Perhydrol" and 1 g. of finely powdered dibenzoyl peroxide. Hydrolysis and steam distillation gave 58 ml. of alcohol (dried by potassium carbonate), which distilled completely at 118–119°, with no evidence whatever of *n*-pentanol-1 (boiling point 137.8°).

**Reaction of Pentene-2 with Sulfuric Acid.**—Pentene-2, prepared as noted above, was treated with a slight excess of 80% sulfuric acid at about 20°, the acid product hydrolyzed and distilled with steam. The dried alcohol, and also a sample of *s*-amyl alcohol made in a similar manner from the amylene fraction of cracked naphtha, were distilled eight times through a small packed column and the following fractions obtained:

| Fraction | B. p., % | From pentene-2, ml. | Amylene fraction, ml. |
|---|---|---|---|
| (1) | 113–114 | 6 | 5 |
| (2) | 114–115 | 32 | 22 |
| (3) | 115–116 | 98 | 59 |
| (4) | 116–117 | 63 | 25 |
| (5) | 117–117.5 | 42 | 22 |
| (6) | 117.5–118 | 54 | 50 |
| (7) | 118–119 | 238 | 340 |

Fraction (3) of each series gave an α-naphthyl urethan which, after several recrystallizations from petroleum ether, melted sharply at 95°, which melting point was unchanged when mixed with the same derivative of synthetic pentanol-3. Fraction (7) gave an α-naphthyl urethan melting at 72° and unchanged when mixed with the derivative made from pentanol-2. This melting point of the naphthyl urethan of pentanol-2 confirms the value given by Gordon and Kremers.[12] However, these authors give the melting point of the α-naphthyl urethan of pentanol-3 as 61–62°. Neuberg and Kramsky[13] give 76–79° as the melting point of this product. Pentanol-3 was prepared by the action of propionic aldehyde on ethylmagnesium bromide, the boiling point of the alcohol being 114.5–115°, as described in the literature. The α-naphthyl urethan was prepared by allowing the mixture of the alcohol and α-naphthyl isocyanate to stand at room temperature for about twenty-four hours.

## Summary

In the reaction of propylene with sulfuric acid, no primary ester is formed. Peroxides do not cause the formation of primary normal amyl hydrogen sulfate from pentene-1. The addition of sulfuric acid, using 85–90% acid to propylene and pentene-1, differs from the addition of hydrogen bromide in forming no primary derivatives. The addition of sulfuric acid to pentene-2 gives sulfuric esters of both pentanol-2 and pentanol-3.

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[11] Levene and Haller, *J. Biol. Chem.*, **79**, 485 (1928).

[12] Gordon and Kremers, *J. Am. Pharm. Assn.*, **16**, 313 (1927).

[13] Neuberg and Kramsky, *Biochem. Z.*, **20**, 445 (1909).

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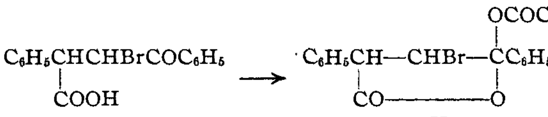
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# The Reactions of Certain Gamma Ketonic Acids. III. Ketonic Beta Lactones

BY E. P. KOHLER, W. D. PETERSON AND C. L. BICKEL

In continuation of the investigation described in the first paper of this series[1] we have studied the second β-bromo acid that is obtained by brominating α-phenyl β-benzoyl propionic acid. Since we are interested primarily in the manner in which ring formation is affected by configuration, we have devoted special attention to a comparison of the conditions under which the two stereoisomeric β-bromo acids are converted into lactones.

In acid solutions these bromo acids, like the unsubstituted ketonic acid itself, form γ-lactones. As nearly as can be determined in reactions which are accompanied by polymerization, there is no conspicuous difference in the ease with which the three acids are converted into these cyclic compounds. The unsubstituted acid forms only an unsaturated crotolactone,[2] but the bromo acids, doubtless because bromine depresses the activity of hydrogen atoms attached to the same carbon atom, form saturated lactones which can be isolated as acyl derivatives



$$\underset{\text{I}}{\begin{array}{l}C_6H_5CHCHBrCOC_6H_5\\ \quad|\\ \quad COOH\end{array}} \longrightarrow \underset{\text{II}}{\begin{array}{l}\qquad\qquad\qquad\qquad\quad OCOCH\\ \qquad\qquad\qquad\qquad\qquad|\\ C_6H_5CH—CHBr—CC_6H_5\\ \qquad\quad|\qquad\qquad\qquad|\\ \qquad\quad CO——————O\end{array}}$$

Although the formation of these lactones involves the generation of a third center of asym-

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[1] Kohler and Kimball, THIS JOURNAL, **56**, 729 (1934).

[2] Anschütz and Montfort, *Ann.*, **284**, 4 (1895); Ref. 1.