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THE SYNTHESIS OF THE ISOMERIC 2-BUTENES[1]

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Introduction

It was necessary to prepare the *cis* and *trans* forms of 2-butene in a pure condition before a satisfactory method of analysis involving the three normal butenes could be developed. The synthesis of 1-butene has already been reported.[4]

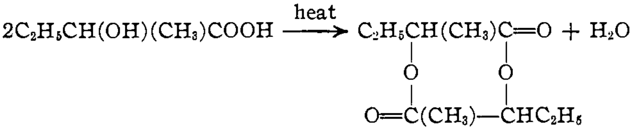
The preparation of the isomeric forms of 2-butene from the two naturally occurring α-methylcrotonic acids, *viz.*, angelic and tiglic acids, has been described by Wislicenus and his co-workers.[5] Since angelic acid is the less stable form, rearranging under the influence of heat or light to the more stable tiglic acid, it is desirable to use a synthetic method which produces as large a yield of angelic acid as possible. The thermal decomposition of α-methyl-α-hydroxybutyric acid[6] serves this purpose. In this work the desired hydrocarbons have been synthesized from methylethyl ketone by the reactions shown in Equations 1, 2, 3, 6 and 7.

$$CH_3CH_2COCH_3 + NaHSO_3 + NaCN \longrightarrow CH_3CH_2CH(OH)(CH_3)CN + Na_2SO_3 \quad (1)$$

$$CH_3CH_2CH(OH)(CH_3)CN + 2H_2O + HCl \longrightarrow CH_3CH_2CH(OH)(CH_3)COOH + NH_4Cl \quad (2)$$

$$CH_3CH_2CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} \underset{\text{angelic acid, tiglic acid}}{CH_3CH{=}C(CH_3)COOH} + H_2O \quad (3)$$

$$CH_3CH_2CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} CH_2{=}C(C_2H_5)COOH + H_2O \quad (4)$$



$$2C_2H_5CH(OH)(CH_3)COOH \xrightarrow{\text{heat}} \begin{array}{c} C_2H_5CH(CH_3)C{=}O \\ \vert \qquad\quad \vert \\ O \qquad\quad O \\ \vert \qquad\quad \vert \\ O{=}C(CH_3){-}CHC_2H_5 \end{array} + H_2O$$ (5)

$$CH_3CH{=}C(CH_3)COOH + HI \longrightarrow CH_3CHICH(CH_3)COOH \quad (6)$$

$$CH_3CHICH(CH_3)COOH + Na_2CO_3 \longrightarrow CH_3CH{=}CHCH_3 + NaI + NaHCO_3 + CO_2 + H_2O \quad (7)$$

In agreement with Wislicenus and his co-workers we obtained the higher boiling isomer from angelic acid and the lower boiling from tiglic acid,

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[4] Lucas and Dillon, This Journal, **50**, 1460 (1928).

[5] Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207–250 (1909).

[6] Blaise, *Ann. chim. phys.*, [8] **11**, 116 (1907).

but the boiling points of our products were somewhat different, being +2.95–3.05° and +0.30–0.40° instead of +2.0–2.7° and +1.0–1.5°, respectively. These workers assigned the *cis* structure to the lower boiling and the *trans* structure to the higher boiling hydrocarbon, whereas Pfeiffer[7] claimed just the reverse. We prefer Pfeiffer's structures and have used them in this paper. We hope definitely to establish the structures by measuring the electric moments of the hydrocarbons and of their dibromides. With bromine at 0° the *cis* hydrocarbon yields a dibromide, b. p. 75.6–75.8° (corr.) at 50.0 mm., and the *trans* yields a dibromide, b. p. 72.7–72.9° (corr.) at 50-mm. pressure. Tentatively we have assumed that the higher boiling dibromide is the racemic and the lower boiling is the meso form, since the recent work of Terry and Eichelberger[8] indicates that when bromine adds to the olefin bond the addition is *trans*. Further confirmation is shown by the fact that in the reaction of these dibromides with potassium iodide in methanol the meso isomer has the higher reaction rate. This agrees with the observation of C. van Duin[9] who found that the meso-dibromosuccinic acid has a higher reaction rate with potassium iodide in 75% ethanol than the racemic.

General Discussion of the Method

In the cyanhydrin reaction (Equation 1) best results were obtained when the procedure usually employed for other compounds[10,11] was modified by using a minimum quantity of water, changing the order in which the chemicals were added and maintaining a temperature of 35° during the reaction. The hydrolysis of the cyanhydrin (Equation 2) should be carried out at temperatures below 90°, since the resulting acid sublimes rapidly at temperatures above 90°.

It is absolutely essential to obtain the α-hydroxy-α-methylbutyric acid in a high degree of purity, since Blaise[6] has shown that when traces of hydrogen chloride are present in the hydroxy acid, the yield of angelic acid is very small. This is due to the catalytic effect of hydrogen chloride upon the rate with which angelic acid is converted into the more stable tiglic acid. In this work a very pure halogen-free product, having a melting point higher than any previously reported, was obtained by a single distillation at reduced pressure. This procedure is superior to the previous tedious method of crystallization from benzene, which must be followed by two weeks' desiccation over solid sodium hydroxide. The yields obtained by different procedures are shown in Table I.

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[7] Pfeiffer, *Z. physik. Chem.*, **48**, 58 (1904).

[8] Terry and Eichelberger, This Journal, **47**, 1067 (1925).

[9] C. van Duin, *Rec. trav. chim.*, **45**, 345 (1926).

[10] Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, **1925**. Preparation 82, p. 151.

[11] "Organic Syntheses," John Wiley and Sons, New York, **1926**, Vol. VI, p. 58.

TABLE I

COMPARATIVE YIELDS OF α-HYDROXY-α-METHYLBUTYRIC ACID

Expt.	NaCN, g.	$NaHSO_3$, g.	Methyl ethyl ketone, g.	Crude cyanhydrin g.	α-Hydroxy-α-methyl butyric acid, g.	Yield, %
5	150	315	216	294	168	47.4[a]
6	165	380	216	314	158	44.5[a]
9	53	126	72	90	56	47.5[b]
11	165	380	216	296	221	62.5[c]
13	165	380	216	320	228	64.5[c]
14	165	380	216	317	219	62.0[c]

[a] Method from "Systematic Organic Chemistry," ref. 10.

[b] Method from "Organic Syntheses," ref. 11.

[c] Method described in this paper.

In the decomposition of the hydroxy acid (Equations 3, 4 and 5) best results were obtained by removing the low-boiling decomposition products from the reaction flask as soon as they were formed. The purification of the resulting angelic and tiglic acids involves a separation from α-ethylacrylic acid, not previously reported as a product of this decomposition (Equation 4). The effect of temperature upon the rate with which angelic acid is converted into tiglic necessitates low-pressure distillations with small quantities of material. By a combination of fractional crystallization and fractional distillation at 12 mm. through a bead column 50 cm. long, angelic and tiglic acids were obtained in a high degree of purity with yields of 20% each. This corresponds to a 40% conversion of the hydroxy acid into the desired products, which is a 6% higher yield than that reported by Blaise.[6]

The reaction of hydrogen iodide[12] with tiglic acid in chloroform solution (Equation 6) proceeded satisfactorily, but the conversion of angelic acid into its hydriodide was difficult since the addition compound slowly isomerized into tiglic acid hydriodide. This change was markedly accelerated by iodine, which must not be present in the chloroform solution of hydrogen iodide. Even though the reaction flask was kept in the dark at 3° during the seven days required for the completion of the reaction, some iodine was formed. The addition of some molecular silver removed the iodine and led to higher yields of the angelic acid derivative. Great care was taken to obtain these two hydrogen iodide addition compounds in a high state of purity since contamination of either one with some of its isomer would result in a mixture of butenes instead of a pure substance.

The decomposition of the above iodo acids into the isomeric 2-butenes (Equation 7) was done in sodium carbonate solution.[5] After the materials were mixed at 5°, gas evolution took place in three distinct stages. As the temperature was slowly raised to 20–30°, carbon dioxide was evolved.

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[12] Prepared by the method of Dillon and Young, THIS JOURNAL, **51**, 2389 (1929).

This was removed from the gas stream by absorption in sodium hydroxide solution. Apparently little or no butene was formed during this first stage. At higher temperatures butene but no carbon dioxide was evolved. Finally, above 60°, the carbon dioxide resulting from the decomposition of the sodium bicarbonate swept the apparatus free from butene. The angelic acid derivative was the more stable, as shown by the fact that the second stage started at 30°, whereas the corresponding temperature was 20° for the tiglic acid compound. A rapid increase in temperature during the decomposition of the angelic acid hydriodide resulted in a yield of butene 20% higher than that previously reported. This result was anticipated since it was assumed that, of the two possible reactions, decomposition and hydrolysis, the former would have the greater temperature coefficient. The yields obtained at the different steps and the physical constants of the various products are shown in Table II.

TABLE II

YIELDS AND PHYSICAL CONSTANTS OF COMPOUNDS

Substance	M. p., °C. (corr.)	B. p., °C. (corr.)	Density *in vacuo*	Refractive index	Yield, %	Overall yield, %
1 α-Hydroxy-α-methyl-butyric acid	72.5	118 (13.0 mm.), 117 (12.5 mm.), 116 (12.0 mm.), 104.5 (7.0 mm.), 93 (2.3 mm.)	....	....	63.0	63.0
2 Angelic acid	45.0–45.5	85.5–87.5 (12–13 mm.)			20.0	12.6
3 Tiglic acid	63.5–64.0	95.0–96.0 (11.5 mm.)			20.0	12.6
4 Angelic acid hydriodide	57.9–58.5	....	....	....	44.5	5.3
5 Tiglic acid hydriodide	86.2–86.3	....	....	....	74.0	8.9
6 Higher-boiling 2-butene from 4 (*cis*)	...	+2.95–3.05 at 746 mm.	....	....	65.4	3.4
7 Lower-boiling 2-butene from 5 (*trans*)	...	+0.3–0.4 at 744 mm.	....	....	84.0	7.5
8 Higher-boiling 2,3-dibromobutane from 6 (racemic)	...	75.6–75.8 at 50.0 mm.	$d_4^{20} = 1.7916$ $d_4^{25} = 1.7836$	$n_D^{20} = 1.5147$ $n_D^{25} = 1.5125$	95.5	3.2
9 Lower-boiling 2,3-dibromobutane from 7 (*meso*)	...	72.7–72.9 at 50.0 mm.	$d_4^{20} = 1.7829$ $d_4^{25} = 1.7747$	$n_D^{20} = 1.5116$ $n_D^{25} = 1.5092$	90.0	6.7

Experimental

α-Hydroxy-α-methylbutyric Acid.—This acid was obtained through the cyanhydrin reaction from methylethyl ketone. Crude methylethyl ketone, b. p. 72–80°, was distilled in a 90-cm. bead column and the fraction distilling at 78–80° was used. In a 3-necked, 3-liter flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel were placed 400 g. of cracked ice, 50 g. of water, 165 g. (3.2 moles) of 95% sodium cyanide and 216 g. (3.0 moles) of methylethyl ketone, b. p. 78–80°. While the solution was being vigorously stirred, 380 g. of sodium metabisulfite (equivalent to 4.0 moles of sodium bisulfite) in 480 g. of water was introduced from the dropping funnel during the course of ten to fifteen minutes. When all but about one-quarter of the solution had been added, the temperature had risen to 35°. A cooling bath of ice and water was then placed outside the flask and a temperature of 30–40° was maintained for ten minutes after the last of the bisulfite had been added. By this time the reaction was finished. The mixture was cooled to 0°, at which temperature the solubility of the cyanhydrin in the salt solution is negligible. The oily cyanhydrin was poured off from the mushy salt layer, 50–100 ml. of water was added to the latter and the additional oil which rose to the top on shaking was again poured off. The crude cyanhydrin, 320–330 g., was hydrolyzed by heating at 90–100° under a reflux cooler with 400 g. of c. p. concd. hydrochloric acid. It was not advisable to heat the solution above 100°, since considerable hydrogen chloride and α-hydroxy-α-methylbutyric acid was lost by volatilization. At the end of seven hours the reaction was usually complete. The solution was cooled to room temperature and without removal of the large amount of ammonium chloride, 100 g. of hydrated sodium sulfate was added. This effects a marked decrease in the concentration of the hydrochloric acid, which is largely converted into sodium hydrogen sulfate and sodium chloride. The solution was cooled to −15° and the mixture of salts was filtered off. The organic acid was not affected by this treatment since its ionization constant is weaker than the second ionization constant of sulfuric acid. Unless the greater part of the hydrochloric acid was removed, the mutual solubilities of this solution and ether were so large that a considerable amount of water and hydrochloric acid dissolved. However, by the procedure adopted a satisfactory extraction of the hydroxy acid by ether could be made. The ether solution was dried with anhydrous sodium sulfate, the ether was distilled off and the α-hydroxy-α-methylbutyric acid was purified by distillation at low pressures. The acid may also be purified by crystallization from petroleum ether at −15°, but this is a more laborious and less satisfactory process since some hydrogen chloride remains in the product. The yield by the distillation method was 64.5% and the material melted at 72.5° (corr.).[13] In Table I a comparison is made of the yields obtained by different methods.

Angelic and Tiglic Acids.—The decomposition of α-hydroxy-α-methylbutyric acid was accomplished by slowly heating approximately 100–125 g. in a 250-ml. round-bottomed distilling flask provided with a 75-mm. bead column in the neck. At a slow rate of heating the decomposition products came over at 150–190°, but if the heating was too rapid considerable hydroxy acid would distil over and the temperature would rise above 190°. It was therefore necessary to heat slowly for a period of one and one-half to three hours in order to allow the slow reaction of decomposition to take place. As soon as no more water distilled, the temperature was raised to 210°, the receiver was changed, and the temperature carried to 240°. A small amount of undecomposed hydroxy acid came over at 210–215°, and considerable lactide at 235–240°. The latter represents 20–25% of the original material. The first fraction, approximately 100 cc., consisted of two phases of approximately equal densities. A separation of the desired unsaturated acids from dissolved water and from the water phase was conveniently accomplished by adding 50 ml. of petroleum ether to 200 ml. of the first distillate (from two decomposition experiments). The petroleum ether solution was dried with anhydrous sodium sulfate and the solvent was distilled off. No attempt was made to isolate any methyl ethyl ketone present. The residue of unsaturated acids was fractionally distilled at 12 mm. through a 50-cm. bead column. The results of the first distillation, as shown in Table III, indicate that a satisfactory separation had been made. After a second distillation at 12-mm. pressure the two main fractions were cooled. Solid angelic and tiglic acids separated out from the respective fractions and were filtered off on a platinum cone from the mother liquor, which was again fractionated.

The angelic and tiglic acids were obtained in a high state of purity by this procedure. The constants are listed in Table II.

From the fraction boiling below angelic acid, α-ethylacrylic acid, m. p. −16°, has been isolated. This material, which has not previously been reported as a product of this decomposition, represents 11% of the original hydroxy acid.

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[13] Boecking, *Ann.*, **104**, 18 (1880), reported 66° and 68°.

TABLE III

UNSATURATED ACIDS FROM DECOMPOSITION OF α-HYDROXY-α-METHYLBUTYRIC ACID; RESULT OF FIRST FRACTIONATION

Fraction	Material	B. p., °C. (corr.)	Press., mm.	Yield, %
1	α-Ethylacrylic acid	76.5–83°	12	11.0
2	α-Ethylacrylic acid and angelic acid	83–85	12	2.0
3	Angelic acid	85–87.5	12	25.0
4	Angelic acid and tiglic acid	87.5–94	12	5.8
5	Tiglic acid	94–96	12	17.0
6	Same and α-hydroxy-α-methylbutyric acid	96–115	12	2.0

The Hydriodides of Angelic and Tiglic Acids.—The addition of hydrogen iodide to the unsaturated acids was carried out according to the general method of Talbot.[5] Since this operation requires careful manipulation, the details of which are not mentioned by Talbot, it is desirable that the procedure developed in carrying out this step be described in detail.

An anhydrous solution of hydrogen iodide (0.6–0.7 *N*) in chloroform was made by passing pure, anhydrous hydrogen iodide[12] into 700 ml. of dry chloroform contained in a 2-liter pyrex distilling flask provided with a ground-glass stopper carrying an inlet tube reaching nearly to the bottom. The chloroform was kept at −15° and the side arm, which constituted the outlet tube, was provided with a drying tube containing phosphorus pentoxide. The concentration of hydrogen iodide was determined at intervals by titrating 2.00-ml. portions against 0.115 *N* NaOH. As soon as the required amount of hydrogen iodide was in solution (53.7–57.7 g.), the unsaturated acid (27.0–29.0 g., dissolved in chloroform) and 1 g. of molecular silver were quickly added. The molal ratio of hydriodic acid to the organic acid should not be less than 1.5 to 1. The outlet tubes of the flask were sealed off in a flame and the ground-glass stopper was tied in and coated with sealing wax. The flask was placed in the dark in an ice box and kept at 3° for seven days. It was then cooled to −15°, the side arm opened, the inlet tube removed and a capillary tube inserted in its place. The flask was heated by a water-bath at 30° and the chloroform was distilled at 20-mm. pressure. Low-temperature distillation was desirable since the decomposition of hydriodic acid and the change of the angelic to the tiglic acid derivative must be kept at a minimum. The residue was extracted at 30–35° with the least possible amount of petroleum ether, b. p. 40–60°, filtered to remove silver iodide and the filtrate was cooled to −15°. The crystalline hydriodide obtained by this procedure was pure when tiglic acid was the starting material but was a mixture when angelic acid was used. In the latter case the mixture contained large quantities of the stable tiglic acid hydriodide. This impure product was extracted twice at room temperature with 5-ml. portions of the petroleum ether and then dissolved at 30–35° in 20 ml. of the solvent. This solution was cooled and three crops of crystals were removed as the cooling progressed. Pure angelic acid hydriodide, m. p. 57.5–58.5°, constituted the first two crops, but the third crop and likewise the material obtained from the crystallization of the 5-cc. extractions were mixtures, as shown by the melting range of 39–52°. Although a small amount of the pure angelic acid hydriodide can be obtained by working up this crude material, it is not practicable to do so.

The Isomeric 2-Butenes.—The butenes were generated in a 3-necked, 3-liter flask provided with a mechanical stirrer, a dropping funnel and an outlet tube. To the latter were attached in series a spiral washing bottle containing aqueous sodium hydroxide for removing carbon dioxide, a calcium chloride drying tube, a receiving tube surrounded by an ice–hydrochloric acid bath at −30 to −35°, a specially designed flask containing bromine for absorbing any uncondensed butene and a drying tube of calcium chloride.

The reaction flask was immersed in a vessel of ice water, 71.5 g. (0.314 mole) of the angelic or tiglic acid hydriodide was placed in the flask and 26.6 g. (0.25 mole) of sodium carbonate dissolved in 650 ml. of water at 5° was rapidly added through the dropping funnel. The liquid was stirred and the temperature of the bath was slowly raised. A lively evolution of carbon dioxide took place at 10° in the case of the tiglic acid and at 15° in the case of the angelic acid derivative. The temperature of the bath was increased as fast as the absorber would take care of the carbon dioxide. This corresponds to a rate of 20 to 30° per hour until 45–50° was reached. At 20° the gas from the tiglic solution and at 30° that from the angelic solution began to pass the absorber, and soon afterward the evolved gas seemed to be nearly pure butene. The temperature was increased more rapidly above 45° since the gas evolution had dropped off. At 65–70° the evolution of carbon dioxide was again rapid and swept the residual butene into the receiver. Practically complete condensation of the butene was accomplished since not more than 1 ml. of dibromobutane was recovered from the bromine absorption flask.

When these hydrocarbons were separately distilled in the apparatus especially designed for this purpose, each distilled completely over a temperature range of 0.1°, as shown in Table II.

The Isomeric 2,3-Dibromobutanes.—These were prepared by slowly distilling the pure butenes into an all-glass reaction flask kept at −15° and adding from time to time small amounts of bromine. After the formation of the first quantity of dibromide the butene was always kept slightly in excess in order to avoid the formation of tribromides. At the end of the reaction, a slight excess of bromine was added to remove the last traces of butene. The products were immediately washed with dilute sodium bisulfite solution, sodium bicarbonate solution and water and were then dried with anhydrous calcium chloride. They were fractionally distilled at 50-mm. pressure in order to avoid the isomeric change which Faworsky[14] noted at more elevated temperatures. The small distillation range of each of the dibromides (Table II) indicates that a single substance and not a mixture of isomers is formed in each case.

Summary

Starting with methyl ethyl ketone, the *cis*- and *trans*-2-butenes have been synthesized in a high state of purity.

Necessary details are given for the preparation and purification of the following intermediate compounds: α-hydroxy-α-methylbutyric acid, angelic acid, tiglic acid, angelic acid hydriodide, tiglic acid hydriodide, the isomeric 2-butenes and the corresponding dibromobutanes.

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[14] Faworsky, *Ann.*, **354**, 325 (1907).